CRANFIELD UNIVERSITY

JAMES VINCENT BARLOW

ACCUMULATION, TRANSPORT AND POTENTIAL TREATMENT OF SURFACE SEDIMENT ON CAR PARKS WITH CHANNEL DRAINS

SCHOOL OF ENERGY, ENVIRONMENTAL TECHNOLOGY AND AGRIFOOD

PhD

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ABSTRACT

Urban pollutants have been identified as a significant source of environmental pollution, posing a risk to human health, the environment, and are toxic to flora and fauna. Highways are recognised as one of the key sources of pollution, from both vehicles, and surrounding infrastructure. A number of studies have investigated accumulation of sediment and the associated pollutants on highways, and the runoff generated as a result of rainfall. Car parks share many potential contributory sources of pollutants with highways, but there is a lack of studies regarding car parks, despite them being identified as a significant percentage of urban land use.

A series of experiments were undertaken in order to develop an understanding of the characteristics of car park sediment. The physical and chemical characteristics of sediment were analysed at different stages throughout the drainage system. Firstly on the sediment accumulated on car park surfaces, followed by that mobilised and transported into a channel drain during simulated rainfall events. Finally, potential treatment of pollutants within sediment in a channel was quantified.

The physical and chemical characteristics of car park sediment was shown to be similar during both the accumulation (build-up) and wash-off stages, suggesting that the accumulated sediment is generally mobilised and transported to the channel drain (wash-off). Furthermore, both the physical and chemical characteristics of the sediment were shown to be similar to those found on highways, thorough the build-up and wash-off phases. Finally, potential treatment of organic pollutants (PAH) by biodegradation was demonstrated, but not comprehensively proved.

Keywords:

Urban Pollution, Wash-off, Runoff, Particulate Matter, Heavy Metals, PAH, SUDS

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LIST OF ABBREVIATIONS

AADT	Average Annual Daily Traffic
AAS	Atomic Absorption Spectroscopy
BS	British Standard
CEH	Centre For Hydrology And Ecology
Cf	Capacity Factor
CIRIA	Construction Industry Research And Information Association
Conc.	Concentration
CSO	Combined Sewer Overflow
DAT	Days After Treatment
DCM	Dichloromethane
EA	Environment Agency
EC	European Commission
EMC	Event Mean Concentration
EPA	Environmental Protection Agency
EU	European Union
FEH	Flood Estimation Handbook
FF	First Flush
FWMA	Flood Water Management Act
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
HEPA	High-Efficiency Particulate Air
HMW	High Molecular Weight
ISO	International Organization For Standardization
LMW	Low Molecular Weight
LOD	Limit Of Detection
LSD	Least Significant Difference
PAH	Polycyclic Aromatic Hydrocarbons
PSD	Particle Size Distribution
PVC	Polyvinyl Chloride
RSC	Royal Society For Chemistry
S.D.	Standard Deviation
SNIFFER	Scotland & Northern Ireland Forum For Environmental Research
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
SUDS	Sustainable Drainage Systems
TPAH	Total Polycyclic Aromatic Hydrocarbon
TPH	Total Petroleum Hydrocarbon
TSS	Total Suspended Solids
uPVC	Unplasticized Polyvinyl Chloride
WFD	Water Framework Directive

1 Introduction

1.1 Background

Pollutants from stormwater runoff have been identified as a significant source of environmental pollution (Brezonik and Stadelmann, 2002; Davis and Birch, 2010). Furthermore, urban pollutants pose a risk to human health, the environment, and toxicity to flora and fauna (Borchardt and Sperling, 1997; Walker et al., 1999; Fu and Wang, 2011). Highways are recognised as one of the key sources of urban pollutant, as are roofs (Sorme, 2003; Gunawardana et al., 2012; Lundy et al., 2012). As such, many studies have investigated the build-up and wash-off of pollutants from the surface of highways, such as Robertson et al., (2003), Carraz et al., (2003), Gunawardana et al., (2012) and Wei and Yang, (2012).

It has been suggested that particulate matter is a major concern with regards to pollutants (Vaze and Chiew, 2004; Bjorkland, 2011), as it acts as a substrate for other pollutants. Sources of particulate matter are wide ranging. Gunawardana et al. (2012) identified industrial emissions, roofing materials, street furniture, litter, spills, erosion of surrounding soils and traffic as the main causes, whereas Herngren et al. (2006) and Thorpe and Harrison (2008) both concluded that traffic is the main cause. The sources can be grouped into ‘vehicle related pollutants’ and ‘infrastructure related pollutants’ as shown in Table 1.1 below, compiled from Sorme (2003) and Westerlund (2005), Thorpe and Harrison (2008) and Gunawardana et al. (2012).

Table 1.1: Sources of Particulate Matter (Sorme, 2003; Westerlund, 2005; Thorpe and Harrison, 2008; and Gunawardana et al., 2012)

Vehicle Related Particulates	Infrastructure Related Particulates
Exhaust Emissions	Soil Erosion
Engine Degradation	Road Material Break up
Anti-freeze	Roadside Gullies
Fuel Spillage	Street Furniture
Brake abrasion/degradation	Roofs
Tyre abrasion/degradation	
De-icing Materials	

Within this particulate matter, one of the main pollutant types is heavy metals. Metals are present in many manufactured items, finding their way into the environment due to usage and wear and tear. Sources of heavy metals can be split in to 'vehicular' and 'non-vehicular' sources, an overview of which are detailed in Table 1.2 below. Of these, vehicular pollutants have been identified as the predominant source of heavy metal pollutants (Sorme, 2003; Thorpe and Harrison, 2008; Ellis and Revitt, 2008; Lundy et al., 2012).

Table 1.2: Vehicle and Non-Vehicle Sources of Heavy Metals (Sorme, 2003; Thorpe and Harrison, 2008; Ellis and Revitt, 2008; Lundy et al., 2012).

Non-Vehicle Sources	Vehicle Sources
Stabiliser in PVC Products	Car Bodies
Stainless Steel	Brake Systems
Long-Life Goods	Tyres
Paints	Road Materials
Concrete	Road Structures/Markings
Treated Woods	
Cable Sheathing	
Galvanised Goods	
Street Furniture	

The other main pollutants identified are hydrocarbons. Traffic has been identified as the primary source of hydrocarbons. This is partly due to fuel combustion, whereby as a result of incomplete combustion, unburned hydrocarbons are emitted (Dong and Lee, 2009; Bjorkland, 2011). Additionally, hydrocarbons can be deposited from vehicles parts, as Thorpe and Harrison (2008) identified that up to 40 % of materials in vehicles can be hydrocarbon based, and also materials from highway infrastructure (Mostafa et al., 2009).

Non-vehicular sources of hydrocarbons have also been identified. Bjorkland (2011) identified a number of industrial materials containing hydrocarbons, including plasticisers, solvents, lubricants, detergents, adhesives, resins, building materials and paints among others.

Currently, car parks have been rarely studied as important sources of urban pollutants. Wicke (2009) and Goonitilleke (2009) included car parks as part of larger studies relating to runoff, but they were not the main focus. This is

surprising, as (Davis et al., 2010) identified that up to 6.5 % of the total urban footrpint may be taken up by car parks.

Whilst car parks and highways both have similar potential as contributory sources, there is potentially great variance in pollutant load and type. For example, vehicular sources have been identified as a key contributor of pollutant (Sorme, 2003; Westerlund, 2005; Escarameia et al., 2006; Gunawardana et al., 2012) from corrosion of metals, to hydrocarbons from oils and lubricants. This may be exacerbated on car parks, as where a car passes, for example, a 1 m^2 section of highway briefly, it may be resident on a car park for hours, possibly days. This opens up the potential for variation, as pollutants may be deposited constantly.

Additionally, tyres and brakes have been identified as major sources of pollutant, both metals and hydrocarbons (Sorme, 2003; Thorpe and Harrison, 2008). The nature of car park usage dictates that manoeuvring and braking is necessary. Within these processes, it is likely that tyres and brakes will be in usage, potentially exacerbating the effect and contribution of pollutant from these sources.

For reasons such as these, car parks have the potential to harbour pollutants, and their importance should not be overshadowed by highways.

Traditionally, in the UK, surface water runoff from highways or car parks was discharged to watercourses, or piped into the sewer system. Legislation such as the WFD (EU, 2000), FWMA (UK, 2010) and the Draft National Standards for SUDS (2015) are pushing towards sustainable drainage. The use of SUDS can provide a degree of treatment in the SUDS treatment train, preventing the pollutants identified above from entering watercourses, or overloading the sewer system and WWTW (Barbosa et al., 2012). In a combined foul water sewer system, this overloading can lead to pollution of watercourses, through discharge from CSO’s. Therefore, SUDS preventing this is a key factor in reaching the water quality goals set in the WFD (EU, 2000).

One of the benefits of SUDS is the facility to provide treatment to runoff, as part of a SUDS treatment train. This is done by processes such as filtration through media, or sediment capture through grassed swales or basins slowing flow and encouraging settlement CIRIA (2007). Biodegradation has also been identified as a method of treating hydrocarbons within SUDS, demonstrated by SNIFFER (2008).

Whilst SUDS have many benefits, one of the negative attributes is the land take, when compared to traditional engineered drainage products. For example, a swale designed to convey the same discharge of water will need to be larger than an equivalent channel drain. This is due to the grassed design of the swale, designed to slow down flow, attenuate and providing a filtering effect for suspended sediment – thus effecting treatment (CIRIA, 2007).

An engineered channel on the other hand, is designed to convey water efficiently, with no apparent treatment. There may be potential for treatment within channel drains, but limited work has been done in this area. Hilliges et al. (2013) devised a 3-stage treatment system, the first part of which included a channel with baffles, followed by two other stages of treatment. The channel itself was not deemed to be the main cause of treatment, functioning more as to convey water and provide potential primary treatment. Furthermore, research concerning treatment on car parks tends to focus on pervious pavement (Pratt et al., 1999; Newman et al., 2005) and other infiltration variants (Puehmeier, 2013).

1.2 Thesis Structure

A conceptual model has been developed, demonstrating the processes and phases involved in the accumulation, transport and potential treatment of surface sediment on car parks with channel drains.

The thesis has been written as a literature review followed by a series of individual papers, the findings of which are brought together in an integrated discussion to answer the research questions devised.

Figure 1.1 illustrates the conceptual model described, identifies which papers address each phase of the model, the objective of each paper, and finally a brief overview of the methodology used to achieve these objectives.

Figure 1.1: Conceptual Model of Thesis Structure

1.3 Research Questions

In order to link the four phases of the conceptual model above, several overall research questions have been devised to guide the project:

1. Do the physical and chemical characteristics of the sediment found on car park surfaces differ significantly with type of use and location and how do they compare with highway sediments?
2. Are the physical and chemical characteristics of the sediment that enters channel drains on car parks during rain-storms of different intensities the same as that of the sediment found on the car park surface?
3. Are the physical and chemical characteristics of the runoff entering the environment from channel drains the same as those of the water entering the drains?

1.4 Research Aim

From these questions, an overall aim has been devised. This is:

To determine the physical and chemical characteristics of sediments found on car parks, the changes in those characteristics during accumulation and mobilisation/transportation, and treatment within channel drains

1.5 Research Objectives

In order to answer the research questions, and achieve the aim above, the following objectives have been set.

1. **Chapter 2 – Literature Review**
   Review current literature to determine the sources of car park pollutant, factors affecting pollutants, and potential treatment methods.

2. **Chapter 3 – Paper 1: *'Characterisation of the Physical and Chemical Properties of Car Park Surface Build-up'***
   Characterise chemical and physical properties of car park surface build-up.

3. **Chapter 4 – Paper 2: '*Investigation into the Effect of Rainfall Intensity on Pollutants Entering a Channel Drain'***
   Quantify the effect of rainfall intensity on mobilisation and transportation pollutants.

4. **Chapter 5 – Paper 3: *'Asssessment of the Wet-vac Sediment Colelction Method as a Representation of Rainfall'***
   Validate the wet-vac collection method as being representative of a rainfall event.

5. **Chapter 6 – Paper 3: *Biodegradation of PAH in Channel Drain Sediment'***
   Identify potential evidence for the biodegradation of PAH in channel drain sediment.

1.6 Methodology Overview

The above objectives will be addressed through four experiments, and then brought together in order to achieve the main aim, and answer the research questions posed. A brief outline of each experiment is as follows:

1. Characterisation of the Physical and Chemical Properties of Car Park Surface Build-up
   - Devise a repeatable method for collection of sediment
   - Analyse heavy metal, PAH and particle size characteristics from a number of car parks

- Examine similarities/difference between car parks of varying location/usage type
- Determine ‘typical’ values for the characteristics analysed if possible
- Compare results of analysis to other studies, and to those found on highways
- Compare results to those found in channel drain sediment

2. Investigation Into the Effect of Rainfall Intensity on Pollutants Entering a Channel Drain
    - Examine the effect of rainfall intensity on car park sediment entering a channel drain
    - Examine the effect of rainfall intensity on pollutant concentrations entering a channel drain
    - Profile pollutant concentrations entering a channel drain over the course of rainfall events of varying intensity
    - Compare the characteristics of runoff entering a channel drains to those of surface runoff

3. Assessment of Wet Vac Sediment Collection Method as a Representation of a Rainfall Event
    - Compare the characteristics of runoff, compared to those obtained from the wet vacuuming of surface sediment

4. Biodegradation of PAH in Channel Drain Sediment
    - Determine whether biodegradation of PAH occurs in channel drain sediment
    - Examine the effect of temperature on biodegradation of PAH in channel drain sediment
    - Examine the effect of PAH concentration on biodegradation of PAH in channel drain sediment
    - Examine the effect of moisture content on biodegradation of PAH in channel drain sediment

2 Literature Review

This chapter contains a review of the current literature regarding urban pollutants, specifically those on car parks and highways. It forms the basis of the 'Source' phase of the Conceptual Model detailed in Chapter 1. This contains the fundamentals of urban pollutants: types, characteristics, sources and processes, all of which form the knowledge base for the proceeding chapters.

Source → Accumulation → Transport → Treatment

The objective of the literature review is to: 'Review current literature to determine the sources of car park pollutant, factors affecting pollutants, and potential treatment methods'.

2.1 Pollutant Sources in Urban Runoff

The urban environment has a multitude of uses, and subsequent potential sources of pollution, from industrial discharges to simple road use. Specific types of pollutants will be identified in future sections, as will their specific sources, with this section focusing on urban pollutants as whole.

In a Highways Agency report, Escarameia et al. (2006) determined that the main causes of urban pollution were construction and maintenance of roads and the vehicles using them. More specifically they identified the following:

- Combustion of fuel
- Corrosion of vehicles
- Corrosion of signage/fencing
- Wear to brakes and tyres
- Wear of pavements
- Herbicides and fertilisers
- De-icing salts and other products used (for cleaning etc.)
- Atmospheric fallout

This list is complimented by many studies identifying major causes of pollution (e.g. Lundy et al., 2012). One of these in which greater detail can be found is *The SUDS Manual* (Woods Ballard et al., 2007), which is intended to be the definitive guide to SUDS in the United Kingdom. Within this, the sources, typical pollutants and further details are provided, drawing information from many other works, such as Wilson (2004). This is reproduced in Table 2.1*,* supplementing it with information found in Lee at al. (2002), Crabtree et al. (2006) and Scholes et al. (2008).

The sources of each pollutant will be explored further in the appropriate section, i.e. Sources of heavy metals, Sources of hydrocarbons. For easy reference and a general overview of urban pollutant sources,

Table 2.1: Sources of Urban Pollutants (Woods Ballard et al., 2007)

Source	Typical pollutants	Source details
Atmospheric deposition	• Phosphorous, nitrogen, sulphur • Heavy metals (lead, cadmium, copper, nickel, zinc, mercury • Hydrocarbons	Industrial activities, traffic air pollution and agricultural activities all contribute to atmospheric pollution. This is deposited as particulates. Rain also Absorbs atmospheric pollutants.
Traffic - exhausts	• Hydrocarbons • MTBE • Cadmium, platinum, palladium, rhodium	Vehicle emissions include polycyclic aromatic hydrocarbons (PAH) and unburned fuel and particles from catalytic converters.
Traffic – wear and corrosion	• Sediment • Heavy metals (lead, chromium, copper, nickel, Zinc)	Abrasion of tyres and corrosion of vehicles deposits pollutants onto the road or car parking surfaces.
Leaks and spillages (e.g. from road vehicles)	• Hydrocarbons • Phosphates • Heavy metals • Glycols, alcohols	Engines leak oil, hydraulic and de-icing fluids and spillages occur when refuelling. Lubricating oil can contain phosphates and metals. Accidental spillages can also occur.

Source	Typical pollutants	Source details
Roofs – atmospheric deposition, bird droppings, corrosion and vegetation	• Heavy metals (copper, lead, zinc) • Bacteria, organic matter	Roof water is often regarded as clean. It can, however, contain significant concentrations of heavy metals resulting from atmospheric deposition or the corrosion of metal roofing or from other coatings such as tar.
Litter/animal faeces	• Bacteria/viruses • Phosphorous, nitrogen	Litter typically includes items such as drinks can, paper, food, cigarettes, animal excreta, plastic and glass. Some of this will break down and cause pollutants to be washed off urban surfaces. Dead animals in roads decompose and release pollutants including bacteria. Pets leave faeces that wash into the drainage system.
Vegetation/land scape maintenance	• Phosphorous, nitrogen • Herbicides, insecticides, fungicides • organic matter	Leaves and grass cuttings are an organic source. Herbicides and pesticides used for weed and pest control in landscaped areas such as gardens, parks, recreation areas and gold courses, can be a major source of pollution.
Soil erosion	• Sediment • Phosphorous, nitrogen • Herbicides, insecticides, fungicides	Runoff from poorly-detailed landscaped or other areas can wash onto impervious surfaces and cause pollution of runoff.
De-icing activities	• Sediment • Chloride, sulphate • Heavy metals (iron, nickel, lead, zinc), glycol • Cyanide • Phosphate	De-icing salt is commonly used for de-icing roads and car parks. Rock salt used for this purposes comprises sodium chloride and grit. It can also include cyanide and phosphates as anti-caking and corrosion inhibitors, heavy metals, urea and ethylene glycol.
Cleaning activities	• Sediment • Phosphorous, nitrogen • Detergents	Washing vehicles, windows, bins or pressure washing hardstandings leads to salt, organic matter and detergents entering the surface water drainage.
Wrong sewer connection	• Bacteria • Detergents • Organic matter	Wrong connections of foul sewers to surface water sewers where separate sewers exist.
Illegal disposal of chemicals and oil	• Hydrocarbons • Various chemicals	Illegal disposal of used engine oils or other chemicals can occur at small (domestic) or large (industrial) scales.

Exploring the sources of pollutant further, Figure 2.1 provides a schematic summary of the 'Source – Pathway – Receptor' model with regards to highway or urban runoff, In this way, the whole process is demonstrated, from the sources, such as roof surfaces and industrial estates through the pathways of highway surfaces, road gully pots and sewers, to the final receptor of receiving water courses. It is here that the WFD (EU, 2000) is concerned, achieving 'good status' for all receiving watercourses by 2015. The schematic is a good resource in visualising, and providing an overview of, the many pollutant sources and their pathways in the drainage system.

Despite referring to highway chambers, the diagram is also directly relevant to car parks. The central box 'Highway surfaces' may also be interpreted as 'Car park' surfaces, as all of the sources feeding in to it may contribute in the same way.

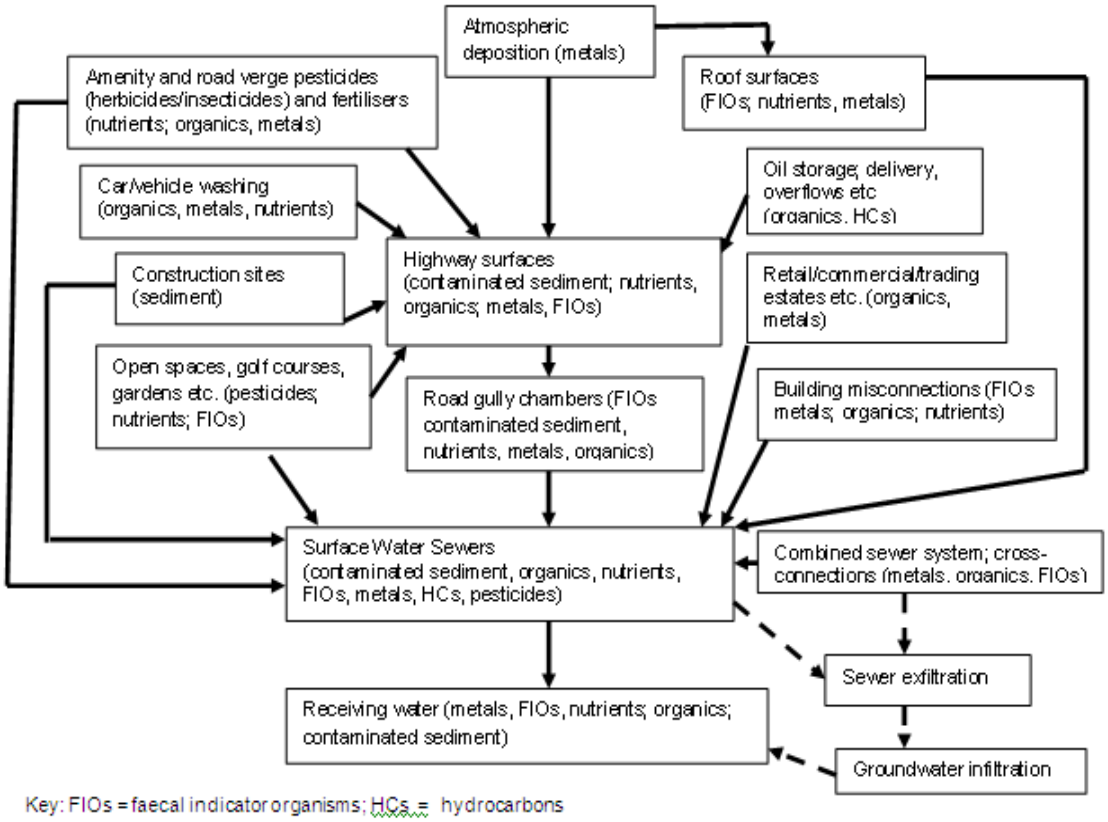

Figure 2.1: Sources, Pathways and Receptors of Urban Pollutants (Lundy et al., 2012)

2.2 Particulates in Urban Runoff

A majority of the pollutants found in urban runoff are either dissolved or particulate. However, many reports such as Vaze & Chiew (2004) and Bjorkland (2011) suggest that the overall urban pollutant load is dependent on particulate loads. This is because the particulate matter acts as substrate for many other pollutants. It is for this reason that pollutant loading can vary, depending on several factors, such as climatic conditions, topographical conditions, in channel/pipe physic-chemical conditions, site use type and surrounding land use, as each of these can affect particle loads. This variation is shown in several studies, such as Vaze & Chiew (2002) which found values ranging from 7.3 – 740 g/m^2 of particulate matter, Gunawardana et al. (2012) which found 0.83 – 7.01 g/m^2 for a variety of land uses and finally Carraz et al. (2003), who found values in the range of 7.3 – 740 g/m^2. As it has been identified that pollutants adsorb to particles, this wide range of particulate matter could lead to large variations in concentrations.

2.3 Sources of Particulates

Sources of urban pollutants as a whole have been outlined in the previous section. However, as particulate matter has been demonstrated to facilitate the majority of urban pollution, it is important to examine the predominant particulate sources. Many of these generic pollutant sources involve particulates, although (Gunawardana et al., 2012) identifies the following sources specifically:

- Industrial emissions
- Roofing materials
- Street furniture
- Litter
- Spills
- Erosion of surrounding soils
- Traffic

Furthermore, studies by Herngren et al. (2006) and Thorpe and Harrison (2008) both concluded that traffic is the main cause. On examination, this broad range of sources can be further grouped into the following: 'Vehicle Related Particulates' and 'Infrastructure Related Particulates'. Table 2.2 below details a number of sources and their subsequent types, compiling information from Sorme (2003), Westerlund (2005) and Gunawardana et al. (2012). Within the 'Vehicle Related Pollutants' category, it is possible to separate once more into sub groups of 'Exhaust Emissions' and 'Non Exhaust Emissions' (Thorpe and Harrison, 2008). In the study, it was concluded that each of these are responsible for comparable loadings of particles and therefore pollutants.

Table 2.2: Sources of Particulate Matter (Sorme 2003; Westerlund, 2005; Gunawardana et al., 2012)

Vehicle Related Particulates	Infrastructure Related Particulates
Exhaust Emissions	Soil Erosion
Engine Degradation	Road Material Break up
Anti-freeze	Roadside Gullies
Fuel Spillage	Street Furniture
Brake abrasion/degradation	Roofs
Tyre abrasion/degradation	
De-icing Materials	

2.4 Particle Size Distribution

Due to the variety of sources of particulate urban pollutants, there is also a wide range of particle sizes present, dependent on several factors such as sediment source, pollutant loads and organic matter present. Mckenzie et al. (2008) reports that this can affect behaviour of the pollutants present, due to variances in processes such as settlement, dissolution and suspension. It is agreed

however that the finer size fractions are the most important when dealing with urban pollutants, which throughout the studies varies from the 60 - 150 µm fractions (Mckenzie et al., 2008; Thorpe and Harrison, 2008).

It was reported by Mckenzie et al. (2008) that in a study on roadside deposits that although a greater mass was comprised of particles > 18 µm, the proportion of those < 18 µm were far greater. Westerlund and Viklander (2006) reported similar trends in a study of rainfall events, with > 65 % of particles in the < 6 µm fraction, 23 % in the 6-9 µm fraction, and < 2 % in the 15-120 µm fractions. Similar findings were reported by Li et al. (2006), which reported that although 90 % of particles from rainfall events were from the < 10 µm fraction, they contributed less than 10 % of the overall mass.

2.5 Particle Size Effects

The importance of the finer particulates is derived from their numbers for a given mass compared to the larger sizes. This effectively equates to a larger surface area for adsorption of pollutants, and subsequently potentially higher loadings for a given mass compared to larger particles. Studies by Herngren et al. (2006) and Dong and Lee (2009) found this was the case, with higher pollutant concentrations present in smaller size fractions. Furthermore, it has been found by Herngren (2006) and Mckenzie (2008) that smaller fractions exhibit different behaviour with regards to mobilisation by rainfall and resuspension, meaning that they have the potential to spread the associated pollutants further than larger fractions.

2.6 Heavy Metals

Heavy metals are a vaguely defined subset of elements displaying metallic qualities, and are one of the main constituents of water pollution. They are naturally formed and naturally present in certain levels in the earth’s crust. However, usage by humans has resulted in the release of heavy metals into the

environment. Problems arising from their distribution can include health problems to humans, but more generally to ecosystems. This is in part due to potential bioaccumulation in watercourses and subsequent deposition onto soils and surrounding habitats.

2.7 Sources of Heavy Metals

Heavy metals are present in many manufactured goods. Degradation of these items over time, through daily wear and tear can facilitate their release and subsequent transportation to paved areas via the air, precipitation or direct contact. Table 2.3 below is a based on a summary of findings from Sorme (2003), which reviewed existing literature, and supplemented by several other sources, including Woods Ballard et al. (2007).

Table 2.3: Sources of Heavy Metals (Sorme, 2003)

Source	Heavy Metals
Motorways/Major Roads	Pb, Zn, Ni, Cd
Urban Roads	Pb, Zn, Cd
Suburban Roads	Pb, Zn
Commercial Estates	Ni
Residential Areas	Cd, Zn, Pb
Roofing	Pb

Examining these sources of pollutant further, the above areas can be split down into specific sources. This is due to many studies (e.g. Sorme, 2003; Thorpe and Harrison, 2008; Ellis and Revitt, 2008; Lundy et al., 2012), identifying road traffic as the predominant source of metals in urban environments, thus meriting a separate table. Table 2.4 summaries findings from the fore-mentioned

studies, and additionally Westerlund (2005) and Woods Ballard et al. (2007). Once again, the sources have been grouped as vehicle and non-vehicle related.

Table 2.4: Vehicle and Non-Vehicle Related Sources of Heavy Metals (Sorme, 2003; Thorpe and Harrison, 2008; Ellis and Revitt, 2008; Lundy et al., 2012)

Group	Source	Metals
Non-Vehicle (NV)	Stabiliser in PVC Products	Cd
NV	Stainless Steel	Cr, Ni
NV	Long Life Goods	Cu
NV	Paints	Cr, Pb
NV	Concrete	Cr
NV	Treated Woods	Cr
NV	Cable Sheathing	Cu, Pb
NV	Galvanised Goods	Zn
NV	Street Furniture	Zn
NV	Road Materials	
NV	Road Structures/Markings	
Vehicle (V)	Car Bodies	
V	Brake Systems	
V	Tyres	

From the list in Table 2.4, the sources of vehicle brakes and tyre treads have been examined further, predominantly in Sorme (2003) and Thorpe and Harrison (2008).

2.7.1 Brakes

Braking systems contain a number of materials, especially metals, for a variety of purposes, such as treatment of discs/other components, lubricants, adhesives and filler. Due to the nature of these parts, brakes are subjected to constant abrasion due to the process of braking by applying force to the discs, meaning that particles of these metals are released into the urban environment. Table 2.5 is compiled from work by Sorme (2003) and Thorpe and Harrison (2008), and summarises the constituent metals found in both brake linings and subsequent brake dust formed as a result of usage.

Table 2.5: Pollutants from Car Brakes (Adapted from Lundy and Wade, 2013) (Sorme, 2003; Thorpe and Harrison, 2008)

Metal	Brake Linings (mg/kg)	Brake Dust (mg/kg)
As	< 2 – 18	< 2 – 11
Cd	< 1 – 41.4	< 0.06 – 2.6
Cr	< 10 – 411	135 – 1,320
Cu	11 – 234,000	70 – 39,400
Ni	3.6 – 660	80 – 730
Pb	1.3 – 199,000	4 – 1,290
Sb	0.07 – 201	4 – 16,900
Zn	25 – 188,000	120 – 27,300
Cu	52,100 – 119,000	
Zn	7,200 – 28,800	
Pb	9,050 – 18,700	
Cr	73 – 151	
Ni	70 – 182	

It is evident from Table 2.5, that there is a huge variation in the values for both the brake linings and the subsequent brake dust formed. This could be due to several factors:

- Brake type: Different types of brake, such as drum or disc brake, differ substantially, so different materials will be present. Additionally, the process in which each of them works may lead to different levels of abrasion and subsequently variation in brake dust values.
- Brake materials: for each type of brake, different manufacturers may use slightly different materials, leading to variety in brake dust loads.
- Driving style: Rougher driving styles/harder braking may lead to increased friction, and therefore potentially more abrasion and brake dust.
- Driving conditions: During bad weather, braking may be more aggressive, leading to increased abrasion.
- Age of car/brakes: Older brakes may be more degraded, and may wear down more easily
- Type of car: Variations on size/ weight of car may affect force needed to stop, hence leading to variation in force, abrasion and dust.

Although the data is a useful source of information, due to the sheer number of variables outlined, it is difficult to isolate a definitive range, as the values vary so greatly, over several orders of magnitude in some cases. Thus, if using specific values from the set, caution must be taken.

2.7.2 Tyres

Tyres on cars are the main points of contact between the vehicle and the road/car park, thus are a major contributor to particulate matter, hydrocarbons, and heavy metals, with degradation of the tyre occurring during movement. Despite being predominantly structured of organic materials (hydrocarbons), several metals such as cadmium, copper and zinc are present in tyre rubber, resulting from addition in the manufacturing process for purposes such as filler

material (RSC, 2007) and reinforcement. Table 2.6 once again summarises findings from Sorme (2003) and Thorpe and Harrison (2008).

The data varies due to the numerous factors having the potential to influence the loadings. Therefore, care must be taken if using specific values from the data. Additionally, there may be the presence of dust picked up from usage, as the studies included used tyres.

Table 2.6: Pollutants from Car Tyres (Adapted from Sorme, 2003; Thorpe and Harrison, 2008, Lundy and Wade, 2013)

Metal	Concentration (mg/kg)
Cd	< 0.05 – 2.6
Cr	< 1 - 30
Cu	1 – 490
Ni	< 1 – 50
Pb	1 – 160
Sb	< 0.2 – 0.9
Zn	430 - 10000

2.8 Sources of Hydrocarbons

Once again, traffic has been widely identified as a major contributor of hydrocarbons in surface build up. This occurs due to fuel combustion, whereby as a result of incomplete combustion, unburned hydrocarbons are emitted in both gas and, more importantly, particulate form, Dong and Lee (2009) and Bjorkland (2011). Other fuel related pollutants regularly observed in urban runoff come from the burning of both petrol and diesel, spilled lubricants, and burning of other materials such as coal or wood, and can take the form of alkanes, alkenes or PAH (Polycyclic Aromatic Hydrocarbons) (Dong and Lee, 2009).

Other than the combustion of fuel, there are several other sources of hydrocarbons related to traffic. These include vehicle related sources, such as brake and tyre materials, and infrastructure related sources, including highway materials (Mostafa et al., 2009). Whilst much of the brake is composed of heavy metals, Thorpe and Harrison (2008) state that up to 40 % of the materials can be hydrocarbon based, in the form of resins used as binders. They also suggested that up to 90 % of tyre materials can consist of rubber hydrocarbons, carbon and associates resins/binders/oils. The remainder is constructed of metal/textile reinforcement. Road materials are generally bituminous and therefore relatively prevalent in urban dusts, as can be seen relative to other sources in Table 2.7 taken from Mostafa et al. (2009).

Table 2.7: Total PAH Concentrations in Pollutant Sources (Adapted from Mostafa et al., 2009)

Source	Total PAHs (mg/g)
Fresh lubricant oil	2926
Used lubricant oil	1428
Asphalt	1596
Auto exhaust	1476
Tyre particles	364

Work has been carried out (Mostafa et al., 2009) in order to attempt to differentiate between pollution sources in a specific location. The existence and distribution of certain alkanes could indicate unburned lubricants or tyre particles to be a major source, whereas the presence of PAH at other sites inferred that unburned fuel from exhaust emissions was the predominant source. This can be seen in Table 2.8, whereby the selected PAH column demonstrates those from combustion.

Table 2.8: Hydrocarbon Loadings on Different Street Types (Adapted from Mostafa et al., 2009, Lundy et al., 2014)

Source	Total PAH (mg/g)
Residential street	32
	35
	27
	76
Heavily trafficked street	304
	320
	379
	295
	283
Fresh lube oil	2926
Used lube oil	1428
Asphalt	1596
Auto exhaust	1476
Tyre particles	364

In addition to traffic based hydrocarbons, Bjorkland (2011) has also identified several other potential sources of hydrocarbons in urban runoff. These are summarised in Table 2.9.

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Table 2.9: Non-vehicle Related Hydrocarbon Sources (Adapted from Bjorkland, 2011)

Plasticisers Solvents	Phtalates
Lubricants Detergents Adhesives Resins Pesticides Paints Concrete Building materials	Alkylphenols
Cables Building materials Textiles	Brominated flame retardants
Flame retardants Plasticisers Sealants	Chlorinated Paraffin

2.9 Typical Pollutant Levels

As mentioned above whilst attempting to develop a definition for ‘Urban runoff’, several studies have been conducted around the world to determine typical concentrations or loadings in highway runoff. The following section aims to collate a number of these, if possible determining a range of typical values for pollutants in urban runoff. Two relevant types of study have taken place in this

vein, those that examine the loadings of pollutants present on highway s or other paved surfaces, and those that examine pollutant concentrations in runoff.

Notably, few of the studies concerned comprehensively examine the effect of surface pollutants and runoff loads, i.e. they look at a concentration of pollutant in a drainage system, but not in relation to the loading of pollutants on the paved surface surrounding it. Whilst other studies such as Egodawatta et al. (2006) and Egodawatta (2008) examine at the effect of factors on concentrations, they do not relate it specifically to loadings on that area. Conversely, studies exist such as those by Vaze and Chiew (2002) and Bris et al. (1999) investigating the contents of highway surfaces, but not the car parks relevant to this study.

Little research appears to have been conducted in this area, with studies by Ellis et al. (1987) and Soonthornnonda et al., (2008) determining an equation for exponential wash-off rate. Soonthornnonda et al., (2008) defined a value 'c' which is a coefficient of transport which can be used to determine the metal removal from a surface. It was found that the removal potential for metals followed a trend found by Ellis et al. (1987) regarding total removal rates of TSS, which was Pb > Ag > Zn > Cu > Ni > Hg > Cd. This is due to the degree of particle association decreasing with each metal.

Below are several of the most relevant examples of data regarding pollutant levels. These have been included in order to provide a scale of reference for future findings.

2.9.1 Runoff Concentration

A majority of these studies involving the monitoring and classification of typical highway runoff concentrations took place in different locations around the world. Studies such as Mangani et al. (2004) and Nie et al. (2008) were based in Central Italy and outside Shanghai respectively, whilst very few concern highways in the United Kingdom. The main, if not only, major study in this area is by Crabtree et al. (2006), the results of which can be found in Table 2.10.

Table 2.10: Average Runoff Concentrations of Selected Sites in the UK (Crabtree et al., 2006)

	% Events	Runoff concentration			Runoff load		
Determinand	detected	LOD	Units	Mean	Maximum observed	Units	Mean/1000 m^2
Copper	**100**	**0.3**	**µg/L**	**41.00**	**242.00**	**mg**	**60.59**
Copper (dissolved)	**100**	**0.3**	**µg/L**	**20.58**	**90.00**	**mg**	**29.04**
Zinc	**100**	**0.6**	**µg/L**	**140.30**	**688.00**	**mg**	**205.30**
Zinc (dissolved)	**100**	**0.6**	**µg/L**	**57.49**	**536.00**	**mg**	**74.09**
Cadmium	100	0.001	µg/L	0.49	5.40	mg	0.61
Lead	**88**	**0.1**	**µg/L**	**23.05**	**178.00**	**mg**	**26.54**
Platinum[a]	3	0.15	µg/L	4.00	120.00	mg	0.86
Palladium	30	0.5	µg/L	0.38	7.00	mg	0.37
Nickel	92	0.01	µg/L	5.31	40.00	mg	9.36
Chromium	90	0.3	µg/L	5.98	49.90	mg	8.48
Simazine	28	0.1	µg/L	0.06	0.90	µg	199.31
Amitrole	0	0.01	µg/L	ND	ND	µg	ND
Glyphosate	**28**	**0.02**	**µg/L**	**0.72**	**17.50**	**µg**	**1142.52**
Diuron	3	0.02	µg/L	0.05	2.02	µg	139.09
Bromacil	7	0.1	µg/L	0.02	0.20	µg	18.39
Atrazine	16	0.1	µg/L	0.02	0.20	µg	14.37
Naphthalene	55	0.01–0.05	µg/L	0.11	4.75	µg	32.26
Acenaphthylene	32	0.01–0.05	µg/L	0.02	0.22	µg	15.18
Acenaphthene	28	0.01–0.05	µg/L	0.02	0.31	µg	30.54
Fluorene	38	0.01–0.05	µg/L	0.03	0.26	µg	24.95
Phenanthrene	63	0.01–0.05	µg/L	0.08	0.80	µg	74.74
Anthracene	55	0.01–0.05	µg/L	0.05	0.39	µg	61.95
Fluoranthene	73	0.01–0.05	µg/L	0.16	1.40	µg	275.92
Pyrene	75	0.01–0.05	µg/L	0.16	1.30	µg	307.56
Benzo(a)anthracene	67	0.01–0.05	µg/L	0.11	1.30	µg	160.59
Chrysene	70	0.01–0.05	µg/L	0.12	1.00	µg	200.34
Benzo(b)fluoranthene	**70**	**0.01–0.05**	**µg/L**	**0.14**	**1.10**	**µg**	**217.00**
Benzo(k)fluoranthene	**67**	**0.01–0.05**	**µg/L**	**0.09**	**0.70**	**µg**	**93.66**
Benzo(a)pyrene	**75**	**0.01–0.05**	**µg/L**	**0.15**	**0.70**	**µg**	**232.27**
Indeno(123)cdpyrene	**63**	**0.01–0.05**	**µg/L**	**0.11**	**0.90**	**µg**	**171.84**
Dibenzo(ah)anthracene	43	0.01–0.05	µg/L	0.07	0.58	µg	77.32
Benzo(ghi)perylene	**50**	**0.01–0.05**	**µg/L**	**0.08**	**0.90**	**µg**	**51.4**
Hardness	100	0.5 mg/L	mg/L	148.80	619.00	g	360.43
Chloride (deicing salt)	**15**	**0.2 mg/L**	**mg/L**	**258.43**	**3120.00**	**g**	**525.73**
BOD	**100**	**1.0 mg/L**	**mg/L**	**6.59**	**31.27**	**g**	**14.17**
COD	100	20.0 mg/L	mg/L	88.62	458.00	g	218.09
TSS	**100**	**1.0 mg/L**	**mg/L**	**114.58**	**1350.00**	**g**	**275.92**
NH_4-N	100	0.05 mg/L	mg/L	0.25	0.73	g	0.55

The study aimed to classify examples of average loadings and their effect on the receiving water courses. Those excessively high, i.e. those contributing to watercourse pollutant level failures are found in bold. Although the results are useful in providing mean values, two issues arise.

- Firstly, the units of mg, rather than mg/kg are inconsistent with other data found, preferring mean mg/km^2 instead. This makes comparison difficult without the raw data.

- Secondly, the results are an average of around 60 sites, which although is excellent for providing ‘typical’ values, once again it makes comparison difficult on a site by site basis.

2.9.2 Surface Loadings

With regards to pollutant loads, or those built up in surface dusts, more relevant data is available. This involves data for both heavy metals and hydrocarbons; particulate matter has been emitted from this section to avoid repetition of statements in the Particulates section.

Table 2.11 provides a summary of data from Robertson et al. (2003), Carraz et al. (2003), Herngren et al. (2006), Wei and Yang (2010) and Gunawardana et al. (2012) regarding the average or typical surface loadings of pollutants in a variety of different environments. The ‘Commercial’ results have been highlighted as they can be identified as most likely to be similar to the car parks relevant to this study, i.e. those containing channel drains.

Examining the tables as whole, the most evident observation is the high variance in values throughout. This is evident both between corresponding values for different land uses, but also in each of them where variation is indicated.

For example, the value for Cr in (Gunawardana, 2012) is 3.26, with a variation of 0.4 mg/kg. Whilst itself a potential variation of approaching 25 %, the corresponding value in Herngren et al. (2006) is 0.023, several orders of magnitude lower. Similarly, in Gunawardana (2012), the values for copper can vary up to 40 mg/kg, on a value of 65.5 mg/kg, nearly 2/3 difference. Again, the Herngren (2006) values are orders of magnitude lower (0.27 mg/kg).

These variations could be for number of different reasons. In the same land use, it is still possible for huge variations in conditions. Other potential reasons for such diversification in results are related to the methodologies of the investigations. For example, sampling techniques may have been different,

leading to different volumes of sediment. Otherwise, different analytical techniques may have been used, or the data interpreted differently.

Table 2.11: Surface Loadings of Metals on Different Land Use Types (Robertson et al., 2003; Carraz et al. 2003; Herngren et al., 2006; Wei and Yang, 2010; Gunawardana et al.,2012; Lundy et al., 2014)

Land Use Type	Metal Conc. (mg/kg)					
	Cr	Ni	Cu	Zn	Cd	Pb
Residential	14.5+/-8.7	7.92+/-5.00	131.4+/-26.0	296.6+/-78.0	0.51+/-0.10	32.5+/-12.2
Industrial	3.96+/-0.40	6.11+/-1.8	65.5+/-20.0	176.4+/-100	0.19+/-0.10	25.7+/-11.0
Mixed	9.37+/-2.30	7.01+/-1.6	98.4+/-24.0	236.5+/-42.0	0.35+/-0.10	29.1+/-4.70
Commercial	3.16+/-0.40	4.53+/-0.07	70.8+/-20.0	90.4+/-23.0	0.54+/-0.10	38.4+/-9.50
Soil	0.00	0.00	8.09+/-2.10	352.9+/-101	0.11+/-0.08	272.1+/-98
Residential	0.012		0.50	1.27	0.002	0.03
Industrial	0.044		0.70	1.70		0.70
Commercial	0.023		0.27	0.38	0.004	0.25
Urban road dusts	51.29-167	23-86.26	94.98-196.8	294.5-1450	1.17-3.77	53.33-408.41
Urban soils	23.1-194.7	27.8-910	23.3-1226.3	65.6-1964	0.15-8.59	28.6-25,380
Urban inner road dust			39–133	402–1016		120—645
Urban outer road dust			32–283	172–2183		25—260
Urban road dust			14-342	65-990		45-1461

Hydrocarbons in urban dusts have been examined in a number of studies, results from which can be seen in Table 2.8 and Table 2.12 below, from Mostafa et al. (2009) and Dong and Lee (2009) respectively.

Although both of the tables above are useful, For example, 3 out of 4 values for residential streets are between 27 – 35 mg/g, save for 1 value at 76 mg/g, which is still in the same order of magnitude. Results for heavily trafficked streets are similarly coherent, ranging from 283 – 320 mg/g, with the exception of 1 result at 379 mg/g, which is once again a rather insignificant variation.

Table 2.12 is arguably more so. This is due to the clear trends present, whereas Table 2.8 is rather generalised, with too many examples with relatively little detail. Table 2.8 however does demonstrate relatively constant values of hydrocarbons for two categories: residential streets and heavily trafficked streets.

For example, 3 out of 4 values for residential streets are between 27 – 35 mg/g, save for 1 value at 76 mg/g, which is still in the same order of magnitude. Results for heavily trafficked streets are similarly coherent, ranging from 283 – 320 mg/g, with the exception of 1 result at 379 mg/g, which is once again a rather insignificant variation.

Table 2.12: Hydrocarbon Loadings of Different Land Use Types (Adapted from Dong and Lee, 2009)

Land Use Type	PAH Conc. (µg/g)
Non-Ferrous Industrial Site	69.32
	11.84
	184.03

Petrochemical Industrial Site	45.53
	73.32
	49.15
Heavily Trafficked	154.64
	67.15
	53.76
Downtown Area	52.45
	245.12
Residential	19.69
	68.73
	48.83

Interestingly, despite the variation, all of the values in Table 2.8 are within a similar range, unlike those previously discovered for heavy metals. Whether this is due to less possible variants for hydrocarbon build up is impossible to say from the data provided, however the above tables provide a useful point of reference for values.

2.10 Variations in Pollutant Loadings

From the previous sections, it is clear that reported pollutant concentrations and amounts can vary by orders of magnitude from the same land use type. For example, amounts of particulates found in highway runoff range from 0.83 – 740 g/m^2 across several studies. This can be caused by a vast range of factors.

Whilst the previous sections show variation in both loadings and concentration, it has been demonstrated by Drapper at al. (1999) that the main factors in determining runoff concentration is the surrounding characteristics. This can be interpreted in the way that the pollutant loading of the surrounding area directly affects the concentration of the runoff. Hence, the majority of the factors this section will examine potential causes of variation in pollutant loadings rather than those affecting pollutant concentration in runoff.

2.10.1 Runoff (Wash-off)

Other than surrounding characteristics, the main exception to this is the effect of rainfall, which directly affects runoff, rather than build-up. Rainfall in general can be subdivided into 3 categories: intensity, duration and volume, of which intensity is the most important. This is due to both the kinetic energy of the droplets and also the turbulence caused by the flow of the rainfall, which increases with intensity. Both higher intensity and increased turbulence have both been found to increase particle mobilisation, as described below.

The ability of rainfall to mobilise pollutants is known as Capacity Factor (Cf), and was investigated and quantified in work by Egodawatta (2007). The study examined the effect of different rainfall intensities on the pollutants, and found the values presented in Table 2.13.

Table 2.13: Capacity Factor (Cf) of Selected Rainfall Intensities (Egodawatta, 2007)

Rainfall Intensity (mm/h)	Cf (unitless)
< 40	0 – 0.5
40-90	Approx. 0.5
> 90	0.5-1

The results show that up to 40 mm/h, Cf increased until reaching a plateau until 90 mm/h. The plateau was reached due to the inability of remaining pollutants to be mobilised by intensities of less than 90 mm/h. This was evident due to the further increases of mobilised pollutants at this point.

Caution should be taken when using the above results, as they used constant rainfall intensities, whereas in reality rainfall events are seldom linear. Findings may differ without a constant application of rainfall and subsequent energy. Limited further work has since been undertaken by Egodawatta et al. (2007) and Brodie (2011). This study used actual storm events rather than simulated rainfall in the previous study; however findings were much less conclusive.

This is the predominant reason for which values attained by studies in countries with different climates, such as Egodawattaet al. (2007) and Wicke et al. (2009) cannot be used accurately. For example, average rainfall intensity was 133 mm/hr for 2 minutes in the tropical climate of the latter of these studies, whereas a realistic UK equivalent would be in the range of 15mm/h for 1 hour.

2.10.2 Build up (Accumulation)

There are a number of factors which affect the loadings of pollutants on highways, all of which are essentially variants within the sources identified in previous sections. The most important is the total solids or particulate matter present on the surface. It is stated (Sartor et al., 1974; Herngren et al., 2006)

that pollutant loadings are directly linked to particulates due to their adsorption potential. In turn, the amount of particulate matter is dependent on the following factors.

2.10.3 Traffic

It has been identified that traffic as a whole, encompassing both vehicles and associated infrastructure, is responsible for a majority of urban pollutants. Therefore, variations in traffic density, calculated as AADT (Average Annual Daily Traffic), are likely to affect pollutants, as a greater number of vehicles would provide a greater number of potential sources of pollutant.

2.10.4 Surface Type

Surface type is another factor which can have influence on the accumulation of pollutants on urban surfaces. This is due to the varying depths and textures occurring between different surface types. These provide different surface areas for pollutants to accumulate on, and deeper surface depths shown in Table 2.14 have been shown to have a higher build up (Gunawardana et al., 2012).

Table 2.14: Average Total Solids from Various Road Texture Depths (Adapted from Gunawardana et al., 2012)

Land Use	Road Texture Depth Range (mm)	Average Total Solids Load (g/m^2)
Residential	0.76-0.92	1.79
		0.81
Industrial	0.93-1.14	3.53
		7.03
Industrial, Commercial and Residential	0.80-0.91	1.39
		0.78
Commercial	0.63-1.11	2.22
		1.75

2.10.5 Land Use

Table 2.11 and Table 2.14 detail findings from Herngren et al. (2006) and Gunawardana et al., (2012) respectively. Both show great variation in the loadings of metals and solids with relation to the usage classifications of residential, commercial and industrial. These variations are in part due to the different processes occurring on each, and the associated activities involved.

Another point to consider when examining the effect of land use with regards to this study are the similarities and also potential differences between highway and car park pollutants. Touched upon in the opening sections, it has been assumed in several studies, and also within this one, that their pollutant profiles will be of a similar composition.

After examining numerous sources throughout this report, a more detailed opinion can be formed. Taking into account the many complex factors at play, it can safely be assumed that the sources of pollutants will be similar for all usage types. Similarly, factors such as surface type or climatic conditions. Slight

differences may occur in the sense that there is increased residence time on car parks, hence increased periods in which oil or other fluid leaks may occur. Also, lower speeds have been suggested to emit more particles, as has starting the engine of a car. This is particularly relevant, as the engine of cars using a car park must be started, guaranteeing that the car park will be subjected to this source, whereas on a highway, the engine will likely already be running.

2.10.6 Climate

Climatic conditions also have a potentially major impact on pollutant build up. In drier climates, the surface loads of pollutant are washed off less frequently than those where rainfall is frequent. Therefore, when rainfall does occur, pollutant levels will be considerably higher. Work has been done in several studies such as Wicke et al. (2009) to quantify this into a model, with the designation ‘antecedent dry period’.

2.10.7 Surrounding Land Use

Surrounding land has not been identified as a significant contributory factor to urban pollutants, as it can be assumed that the predominant land is built up. Should the land be rural, the potential for airborne particulate matter to be deposited increases, as the ground is not covered/paved as in an urban setting. As a result of increased potential for particulates, the potential for pollutant load also increases, due to adsorption of pollutants to particles.

2.10.8 Timing

The timing of when samples are taken can also affect overall chemical composition. Whilst this could relate to factors such as time of day and associated traffic, or time after a rainfall event, these are covered in other section. This section refers more to the seasonal timing of sampling, with

several studies such as Mangani et al. (2004) and Westerlund (2005) highlighting the potential differences between seasons. Table 2.15 below is a sample from the latter, with great variation in results evident.

Table 2.15: Seasonal Variation of Metal Concentration (Mangani et al., 2004)

	Summer campaign				Autumn campaign			
	Site 1		Site 2		Site 1		Site 2	
Element	Can A	Can B	Can A	Can B	Can A	Can B	Can A	Can B
Al	305.76	158.48	145.52	176.85	90.02	56.24	64.82	313.80
Zn	132.95	86.08	125.30	88.00	0.00	13.00	10.00	0.00
Fe	50.87	29.35	76.31	39.13	101.00	93.00	95.00	96.00
Cu	85.93	6.33	10.20	28.29	13.91	18.26	18.47	15.00
Pb	1.11	3.70	2.50	3.77	0.00	0.00	0.00	0.00

2.10.9 Summary

Due to the reasons for variation identified, especially antecedent dry period, topography or climatic factors, when using data for comparison, care should be taken to consider their potential effects.

Additionally, in the variations observed are reasons for possible differences between highway and car park runoff, such as land use and traffic. It is for this reason that many of the studies cannot be used as comparators for this study involving car parks.

2.11 Pollutant Characteristics

It is evident that particle sizes have a controlling effect on pollutant loadings and concentrations. Studies have also suggested that specific pollutants can be associated with certain particle size fractions. Table 2.16 summarises findings

by Herngren et al., (2006), with those from commercial sites highlighted, for these are likely to bear most relevance to car parks for reasons previously given.

Table 2.16: Particle Size Fraction Association of Metals (Herngren, 2006)

Particle Size (µm)	Land Use	Zn	Pb	Cu	Cd	Cr
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
< 0.45	Residential	0.39	nd	0.08	nd	nd
	Industrial	0.18	nd	0.01	nd	nd
	Commercial	0.83	0.01	0.12	0.003	nd
0.45-75	Residential	1.80	0.04	0.56	0.002	0.02
	Industrial	2.32	0.96	0.96	nd	0.06
	Commercial	0.42	0.34	0.26	0.002	0.03
76-150	Residential	0.72	0.03	0.48	0.002	0.01
	Industrial	0.11	0.04	0.04	nd	0.003
	Commercial	0.30	0.19	0.24	0.01	0.02
151-300	Residential	0.29	0.01	0.68	0.001	0.01
	Industrial	0.04	0.01	0.04	nd	0.002
	Commercial	0.11	0.09	0.53	nd	0.01
> 300	Residential	0.14	0.01	0.34	0.001	0.01
	Industrial	0.08	0.02	0.04	nd	0.01
	Commercial	0.06	0.03	0.22	nd	0.01

From Table 2.16, it is evident that the following suggestions can be justified, as all of the metals are more prevalent in a certain size fractions, ranging from just under 100 % greater than the second highest, to over 7 times greater. The relationships between metals and particle sizes are as follows:

1. Zn is most prevalent in the < 0.45 µm fraction at 0.83 mg/kg, reducing with increasing particle size, with a minimum value of 0.11 mg/kg in the 151-300 µm fraction.
2. Pb is most prevalent in the 0.45-0.75 µm fraction at 0.34 mg/kg, reducing with increasing particle size, but with minimal presence (0.01 mg/kg) in the < 0.45 µm fraction.
3. Cu is most prevalent in the 151-300 µm fraction at 0.53 mg/kg, with similar values (0.24-0.26 mg/kg) in the 0.45-150 µm fractions, and a minimum 0.12 mg/kg in the < 0.45 µm fraction.
4. Cd is most prevalent in the 76-150 µm fraction with a value of 0.01 mg/kg, with similarly small amounts (0.003-0.003 mg/kg) present in fraction sizes below 75 µm and none detected in the > 300 µm fraction.
5. Cr is most prevalent in the 0.45-0.75 µm fraction at 0.03 mg/kg, reducing linearly to 0.01 mg/kg in the > 300 µm fraction, but none detected below 45 µm.
6. In general, the 0.45-0.75 µm fraction contained the most consistently higher average loadings of metals when compared to the other fractions.

McKenzie et al. (2008) conducted a similar study. However, it was found that for all metals, concentration increased as particle size decreased, the equivalent of < 45 µm in Herngren et al., (2006). Further work could be carried out in order to examine this, as insufficient data/information is available from these studies to examine the potential factors influencing the results. It can be determined from both studies however, that metals are predominantly associated with the smaller < 100 µm particle size fractions.

2.12 Pollutants in Legislation

2.12.1 WFD Priority Pollutants

Priority pollutants is a term used widely, the most important instance of which is in the WFD (EU, 2000). This sets out a list of 33 pollutants which should not be present in water courses. Other equivalent terms also exist to describe lists of the same principal, the most prevalent being ‘key pollutants’.

The background for this list came about from *The Groundwater Regulations (EA, 1994)* in which there were two categories of pollutants, List 1 and List 2. These were categorised based on permission to discharge the chemical into watercourses without prior treatment, with list 1 being allowed under certain conditions, and list 2 being prohibited.

Despite the lists, especially ‘Priority Pollutants’ being an extensive collection of pollutants, in the application of examining treatment in channel drains and other engineered drainage products not all are relevant. For example, it is widely agreed that total solid loadings, or TSS concentrations are the key pollutant. This is due to reasons explored previously, in that the solids act as adsorption media for other pollutants (Sartor et al., 1974), with higher solids concentrations leading to relative pollutant levels.

2.13 ICRCL Trigger Concentrations and CLEA Soil Guideline Values

Whereas guidance such as the WFD ‘Priority Pollutants’ list (EU, 2000) specify a complete absence of pollutants, other guidance provides information on concentrations of pollutants. The Interdepartmental Committee on the Redevelopment of contaminated Land (ICRCL) Guideline Values (ICRCL, 198) provide guideline values from various contaminants. These values have since been superseded by the ‘CLEA derived soil guideline values’. Both of these sets of values for the main metals identified are detailed in Table 2.17 below.

Table 2.17: ICRCL and CLEA Values

ICRCL 59/83 Trigger Concentrations				CLEA Soil Guideline Values (SGV)	
Contaminant	Planned Use	Trigger Value (mg/kg)		Function of Land Use	SGV (m/kg)
		Threshold	Action		
Cadmium	Domestic gardens/alloments	3	-	Residential	10
				Allotment	1.8
	Parks, Playing fields, open space	15	-	Commercial	230
Chromium	Domestic gardens/alloments	25	-	Residential	130
				Allotment	200
	Parks, Playing fields, open space	No limit	No limit	Commercial	5000
Copper	Any uses where plants are grown	130	-	CLEA	130
Lead	Domestic gardens/alloments	500	-	Residential w/ plant uptake	450
				Residential w/o plant uptake	450
	Parks, Playing fields, open space	200	-	Commercial	750
Nickel	Domestic gardens/alloments	70	-	Residential	130
				Allotment	230
				Commercial	1800
Zinc	Domestic gardens/alloments	300	-	CLEA	300
PAH	Domestic gardens/alloments	50	500	-	-
	Parks, Playing fields, open space	1000	10000	-	-

Within the ICRCL guidelines, values are split in to ‘below threshold’, ‘above action’ and ‘between threshold and action’ levels, with the level of remediation dependent on value. Land usage type is also taken into account, with ‘Planned Uses’ split between ‘Domestic gardens, allotments’ and ‘Park, playing fields, open space’, the latter of which having a generally higher threshold.

The CLEA Soil Guideline Values (SGV) are split into either residential (with or without plant uptake), allotment and commercial land use functions, or just a general ‘CLEA’ value. These values are the best of the two sets to use for comparators in this study, as they are more recent, and the ‘commercial’ values are more specific to this project, which focuses predominantly on commercial premises – supermarkets.

Another perspective is by the Environment Agency (2012), who use TSS, Cu, Zn and TPH to determine pollutant levels. The justification for this is similar, that these act as indicators for overall levels of pollution, and that by introducing treatment to address these, others will also be eliminated.

2.14 First Flush Phenomenon

The *First Flush Phenomenon,* can be defined as *'the initial period of stormwater runoff during which the concentration of pollutants is substantially higher than during later periods'* (Lee et al., 2002). This can be explained by the first two stages in the pollution generation and runoff process (Deletic and Maksimovic, 1998) which involves: 1. The build-up of pollutants etc. on the paved area during dry spells, followed by 2. The wash-off of this build-up during a storm event. In summary, it is the high concentration experienced due to a prior build-up caused by a dry spell, rather than pollutants being routinely washed off by regular rainfall/storm events.

An example of the potential difference between the first flush and the EMC (Event Mean Concentration – average of pollutant concentration throughout the duration of a rainfall event) can be found in (Wicke, 2009). Using TSS for reference, great variation can be seen between these values. For example, the results from 28/03/07 show FF values of 38 mg/l, compared to an EMC of 16 mg/l, over double, and those from 24/08/07 show over 4x the concentration in the first flush compared to the EMC, with 120 and 29 mg/l respectively.

Despite this event being commonly accepted (Deletic & Maksimovic, 1998), there is no pattern other than it being the peak of concentration, this can vary due to parameters such as area involved, length of preceding dry period and intensity of rainfall (Lee et al., 2002). There are however, some studies such as Bach et al., (2010) which dispute the existence/importance of a 'first flush'. The reasoning behind these for the most part is the number of variables previously identified makes it difficult to devise a general formula or even trend in occurrence.

However, potentially the most important opinion with regards to this project or SUDS in general, is the view taken by the Flood Water Management Act (2010) and more specifically the Draft National Standards for SUDS. Within these standards contain a clause which states the requirement that runoff generated from the first 5mm of a rainfall event must not be discharged, and must be retained on site or treated there. From this, and suggestions from CIRIA (2006)

and Woods Ballard et al., (2007) that with regards to best practice guidance, it can be assumed that a first flush whereby there are higher levels of pollutant present in the runoff from the first 5 mm of rainfall during an event.

2.15 Treatment in Channel Drains

2.15.1 Introduction to Channel Drains

Sustainable drainage systems (SUDS) have been introduced in the Introduction chapter. The majority of these are 'green' SUDS, such as attenuation basins, or grassed swales, which provide quantitative, qualitative and amenity benefits, but have a large land take. It was also explained why it would be beneficial for channel drains to function as a form of sustainable drainage.

Channel drains are narrow drainage channels, usually 100mm wide, that are widespread on commercial, industrial and, to a lesser extent, residential car parks. Their primary function is to convey surface water on a site level, to either and outfall, or into a surface water/combined sewer system. It is for this reason that they are not classified as SUDS – i.e. whilst providing a quantitative benefit, they do not provide qualitative, ecological or amenity benefits as described in the SUDS triangle.

Other forms of SUDS provide similar functions with regards to water quantity, whilst incorporating the other benefits. For example, swales convey water in a similar way, whilst providing treatment via sediment removal when filtered by grass at low flow velocities, and ecological benefits by providing potential habitat, whereas channel drains are often designed to be self-cleaning, and are a hard engineered material product. Filter strips are designed to filter sediment out of runoff through various layers of filtration media, as opposed to the channels, which are designed for unrestricted flow.

2.15.2 Permeable Pavements

Whilst is has been identified hat little research exists regarding treatment in channel drains, research has been carried out in similar areas which may be relevant. One of these area is gully pots, which receive surface water drainage before conveying it to the sewer. These are not explored in detail, as they are an enclosed system, and do not receive and convey water in the same way channel drains do.

The other field in which similar relevant research has been carried out is permeable (or pervious) pavements. Permeable pavements are used predominantly on car parks for drainage, either by allowing water to permeate through and infiltrate onto the ground, or be conveyed to sewer systems via the pore spaces in the underlying sub-base.

In addition to the qualitative function, permeable pavements are also designed to provide treatment. The main mechanism by which they achieve this is filtration, through the permeable top layer, the pore spaces in the aggregate sub base, and (where possible) infiltration in to the ground. This predominantly treats sediments, and the associated metals due to the association between them.

However, other methods of treatment in permeable pavements have been identified. The process of biodegradation has been identified as a possible form of treatment in SUDS. Several studies (including, but not limited to Pratt et al., 1999; Newman et al., 2004, 2005) have studied the effects of biodegradation in pervious pavements, generally finding that reduction of PAH concentration occurred. This was developed further by Puehmeier (2005, 2013), who used a floating mat with an oil degrading biofilm in infiltration systems to further increase biodegradation

By effecting treatment in this way, the permeable pavement prevents the pollutants from reaching watercourses/sewer systems, and effectively providing treatment. Due to the similar function of channel drains – i.e. site level

conveyance – it may be possible to effect similar methods of treatment with minor modifications.

2.15.3 Treatment in SUDS Sediment

SNIFFER (2008) is the most relevant study with regards to treatment in channel drains. This is because it focuses on treatment in retained sediment from SUDS, and it has been established (Lundy et al., 2014) that channel drains retain sediment. It is considered more relevant than the permeable pavements as it focuses purely on the sediment/soil, whereas permeable pavements include filtration, and the flow in constrained.

The SNIFFER (2008) report also has limitations, with a self-proclaimed aim of delivering *á body of evidence on the behaviour of contaminants in SUDS which have a soil/vegetation base'* i.e. green or soft engineered SUDS.

The aim of the part of the study relevant to this project is a laboratory scale experiment to assess degradation of hydrocarbons. In order to do this, 8 batches of soil were dosed with known quantities (between 3500 and 10000 mg/kg) of PAHs and incubated. Samples were removed at specified time intervals and measured for remaining PAH concentrations. Also included were 2 control batches containing sterilised soil in order to measure natural degradation. Each of the batches was divided into 60 and three bottles were removed at the 0,1,3,7,14,28,42 and 60 day intervals from each batch and assessed for the following parameters:

1. Moisture content – in order to examine the effects compared to the filling and draining of swales and basins, leading to both aerobic and anaerobic conditions.
2. Temperature – in order to simulate the effect of the seasons, as temperature is a major factor on microbial activity.
3. Pollutant concentration – in order to simulate varying pollutant loads in roadside applications. Levels were chosen to reflect concentrations found in in-situ road side SUDS.

4. Bioactivity of Soil – to measure degradation due to chemical and physical processes.

Table 2.22 and Table 2.23 show the concentrations and characteristics of the pollutants added to the samples.

Table 2.17: SNIFFER Report Soil Test Batch Data (SNIFFER, 2008)

Soil Test Batch	Temperature (°C)	Moisture content (%)	Pollutant applied	Pollutant conc mg kg^{-1}
1	15	40	PAH	15
2	5	40	PAH	15
3	15	40	PAH	30
4	15	90	PAH	15
5	15	40	Oil	3500
6	5	40	Oil	3500
7	15	40	Oil	10000
8	15	90	Oil	3500
9*	15	40	PAH	15
10*	15	40	Oil	3500

* Sterilised soil

Table 2.18: SNIFFER Report PAH Details (SNIFFER, 2008)

PAH applied	Abbreviation	No. of rings	Classification
Naphthalene	NAP	2	LMW
Fluorene	FLU	2	LMW
Phenanthrene	PHE	3	LMW
Anthracene	ANT	3	LMW
Benzo[a]anthracene	BAA	4	HMW
Chrysene	CRY	4	HMW
Benzo[a]pyrene	BAP	5	HMW
Dibenzo[a,h]anthracene	DBA	5	HMW
Benzo[g,h,i]perylene	BGP	6	HMW

The study found the following conclusions for each of the variables investigated:

Concentration: The study showed that the higher the starting concentration of PAHs the lower the percentage reduction. This is shown in Table 2.24, where a

PAH concentration of 30 mg/kg compared to 15 mg/kg had a lower total PAH reduction by 19 %.

Table 2.19: Effect of Concentration of TPH Concentrations (SNIFFER 2008)

	% applied dose reduced after 44 days		
	ΣPAH	LMW	HMW
Batch 1 (standard)	49	86	27
Batch 3 (higher PAH conc.)	30	75	3

Moisture Content: It was found that whereas a higher moisture content (90 % compared to 40 %) had a negligible effect on LMW reduction, in HMW hydrocarbons the effect was drastic. Table 2.25 shows the comparison, whereby HMW reduction was 0 % after 44 days, suggesting high moisture content can completely prevent loss of HMW PAH from soils.

Table 2.20: Effect of Moisture Content on PAH Concentrations (SNIFFER, 2008)

	ΣPAH	LMW	HMW
Batch 1 (standard)	49	86	27
Batch 4 (higher % moisture)	28	84	0

Temperature: Results showed that temperature variation has a great effect on PAH reduction. At increased temperatures, both HMW and LMW hydrocarbons were significantly reduced, as shown in Table 2.26, where total PAH reduction was 20 % greater in the sample incubated at 15 ^{o}C opposed to that at 5 ^{o}C. It was also concluded that whereas less reduction of LMW at 5 ^{o}C was likely to be caused by lower rated of microbial activity, the HMW difference seemed to be influenced by other factors, such as limited evaporation compared to 15 ^{o}C.

Table 2.21: Effect of Temperature on PAH Concentrations (SNIFFER, 2008)

	% reduction		
Temp	ΣPAH	LMW	HMW
15C	49	86	27
5C	29	69	6
Sterile soil	25	22	26

2.15.4 Microbial Activity

In order to examine the effect of any microbial activity in the study, results from the sterile soil were compared with the others. The data in Table 2.26 show that temperature has an effect on both HMW and LMW reductions, however, that in LMW is much greater. Results showed that LMW PAH were degraded rapidly, with a significant reduction within hours, compared to a gentle reduction over the course of the study in sterile soil.

However, it was concluded that it may have been possible that the parent compound was transformed into a 'daughter product', which would be transformed further in order for complete biodegradation to have taken place. This may explain the rapid decline in LMW PAH concentration, compared to the HMW PAH, which is less bioavailable.

2.15.5 Summary

Findings from this study suggests that treatment in channel drains may occur for several reasons. Firstly, the concentrations used in the study were based on forms of SUDS, which it can be assumed receive a similar loading of pollutants to channel drains due to similar sources. Therefore, this suggests that with regards to concentration, biodegradation is a possibility.

Secondly, the findings of the moisture content also suggest potential comparison with channel drains. This is since it is not always raining, thus the moisture content of sediment in the channel drains will not be permanently

excessively high. It was found in this study that lower moisture contents were preferable for degradation of both LMW and HMW PAHs.

Finally, an assumption can be made based on the results of this study that there may be comparable bioactivity of soil in channel drains. Once again this is due to the likelihood that the characteristics of the sediment used in this study will not vary substantially due to the comparable nature of function and locations.

2.16 Urban Runoff – Highway Runoff Vs. Car Park Runoff

One key observation that can be made is a distinct lack of studies focusing specifically on car park runoff. The sole study identified was by Wicke et al., (2009), which determined a rainfall contaminant relationship model for Christchurch urban catchments. The input for this model was in fact a car park, and in designing the model provided an example of concentrations of TSS, Cu, Pb and Zn.

Although these results are relevant to car parks, and are reasonably comprehensive, they are inadequate to solely base this investigation on for a number of reasons. Firstly, one study is simply not sufficient, due to the number of possible variables. Specific variables include location of the study, New Zealand, which experiences different climatic conditions to the UK, which may be non-representative results. Additionally, the car parks sampled were all found in one locality – a university campus – whereas a variety of uses would be desirable.

Goonetilleke et al. (2009) also provide limited data on car park runoff. Although this may be useful in contributing to an overall comparison, the car park was merely one of several sample areas (the rest being roads), so once again, the data is not extensive enough to be of sole importance. Wei and Morrison (1994) conducted analysis and monitoring of car park between 1984 and 1991, examining fractional size associations of pollutants. Although clear trends were found, the study is not directly comparable to 2012, as over the time period since, many advances have been made in vehicle manufacture and materials.

Finding a similar lack of data, Wicke et al. (2009) used highway data from Drapper et al. (2000), Gnecco et al. (2005) and Kayhanian et al. (2007) in order to provide a comparison. Due to the similarity in usage between highways and car parks, and using Wicke et al. (2009) as a precedent, it can be assumed that values for pollutant concentrations on car parks will be of a similar value to highways.

In order to avoid confusion in this matter, a blanket term of Urban Runoff will be used later is this project. This is based on the similarities observed between highway and car park runoff when uses are examined, and the precedent set by other studies, due to a lack of data.

2.17 Conclusions

2.17.1 Overview

One of the principal observations from the literature review is the lack of studies and data regarding car park pollutants and the subsequent runoff generated. It was found that a wealth of similar research based on highways existed, and that the principles were interchangeable. However, the study found many potential factors that may lead to discrepancies between the two, predominantly variations in pollutant concentrations between various land uses. It is because of this that further investigative work regarding car parks is recommended.

2.17.2 Types of Pollutant

Pollutants in urban runoff can be split into 3 groups: particulate matter, metals and hydrocarbons. Each of these poses a potential threat to human or environmental health, and management of all 3 groups is a key part of legislation such as the WFD (EU, 2000) and FWMA (2010). Furthermore, the legislation focuses on a list of 33 priority pollutants deemed to be the most important in terms of eradication, which is in the terms of the EU WFD. Additionally, particulate matter or total solids is identified an important pollutant

for its use as an indicator of overall pollution, as pollutants are adsorbed to particulate matter.

2.17.3 Sources

A number of sources for each of the above pollutant groups were identified. Although these are different for each, traffic is a major contributor to all types. This includes exhaust related pollutants including particulate matter, metals from engine component use and hydrocarbons from combustion processes. Non-exhaust pollutant sources from vehicles included tyres and brakes, coming about from particulate matter caused by friction and abrasion of both due to their use. Metals are present in brake materials and also in tyres for the purposes of strength and reinforcement. Hydrocarbons are present in brakes in the form of binder and adhesives, and formed the bulk of the tyre in the form of rubber.

Non-vehicular traffic based sources of pollutants were also identified, coming instead from infrastructure. Contributors to this include signage, roofs, auxiliary structures (e.g. bridges) and road furniture, which are all a source of metals, whilst highway surfacing materials are a key source of hydrocarbons, being predominantly bituminous.

Other sources include particles from degradation of buildings and other infrastructure and industrial process via precipitation or airborne deposition. Additionally, hydrocarbons can be present in many manufactured goods, and for uses such as plasticisers, binders, fillers and flame retardants. Similarly, metals are present as reinforcement in a variety of manufactured goods and processes.

2.17.4 Variations

A key observation was the potential high variability of urban pollutant loadings and concentrations. Many factors can contribute to this variation, affecting both

the amounts in surface dust build up and the associated runoff. Variables include traffic density, surface type, land use, climatic conditions, surrounding land use and timing of data, such as the effect of seasons and rainfall event/storm characteristics. Rainfall intensities, durations and frequencies are a primary variable, and as such capacity factor (Cf), the potential for mobilising sediments and antecedent dry period has been built into accumulation and wash-off models in the form of exponential equations.

2.17.5 Typical Concentrations

The key finding when exploring the typical concentrations of runoff was, as summarised earlier, the lack of data involving car parks, and thus, values for highway runoff were used instead. For the reasons detailed in the previous section, much variation exists between the data from different studies. Of these, the main variable is the location of the study, and the subsequent impacts of differing climatic conditions, traffic behaviour and industrial processes.

Despite the range of values found, the sources can be used to compare any results obtained. With a range of factors considered, an appropriate comparison is possible, with values expected to be in the same order of magnitude.

2.17.6 Characteristics

Despite the discovery of variation within concentrations and loadings of pollutant particles, similarities occur in other areas, one of which is in relation to particle size distribution. Smaller (< 75 µm) particles contributed to approx.. 10 % of the volume, but 90 % of the particle numbers. This is important, as it has been found that pollutants are generally associated with this smaller fraction, due to the increased surface area per given volume.

It was found that research has been done into particle size association with regards to metals. Almost all metals showed a particular affinity to a certain size fraction, which is useful because by analysing particle size data, a reasonable

assumption can be made as to the pollutant load composition. There is however little information regarding hydrocarbons and particle size association.

2.17.7 Treatment

Once again, there was a lack of research on treatment in channel drains. However, research into similar concepts with regards to different forms of SUDS exists. This involved a study into biodegradation of PAHs in SUDS, which comprised of a lab study over a number of months.

Microbial activity is a major influence on percentage reduction of PAHs, occurring at a much higher rate in LMW PAHS than HMW PAHs. Other findings include increased percentage reduction at higher temperatures, a lack of reduction at higher moisture content and reduced PAH reduction in higher initial concentrations.

Many similarities exist between the SUDS concerned and channel drains, such as source of pollutant and general settlement, however so do several differences. For example, SUDS are designed to capture sediment whereas channels are predominantly self-cleaning. It is for this reason that it would be recommended for equivalent studies to take place using sediment captured from channel drains.

2.17.8 Conceptual Model of Car Park Pollutant Systems

In order to display the processes involved in urban pollution on car parks, a ‘conceptual model’ has been developed as part of the initial phase of this present study. This provides a visualisation of the overall process, from deposition of pollutants to entry into the environment. The model can then be used to identify the areas of interest, and inform the research questions to be answered, and the aim to be achieved. The model is shown in **Error! Reference source not found.**.

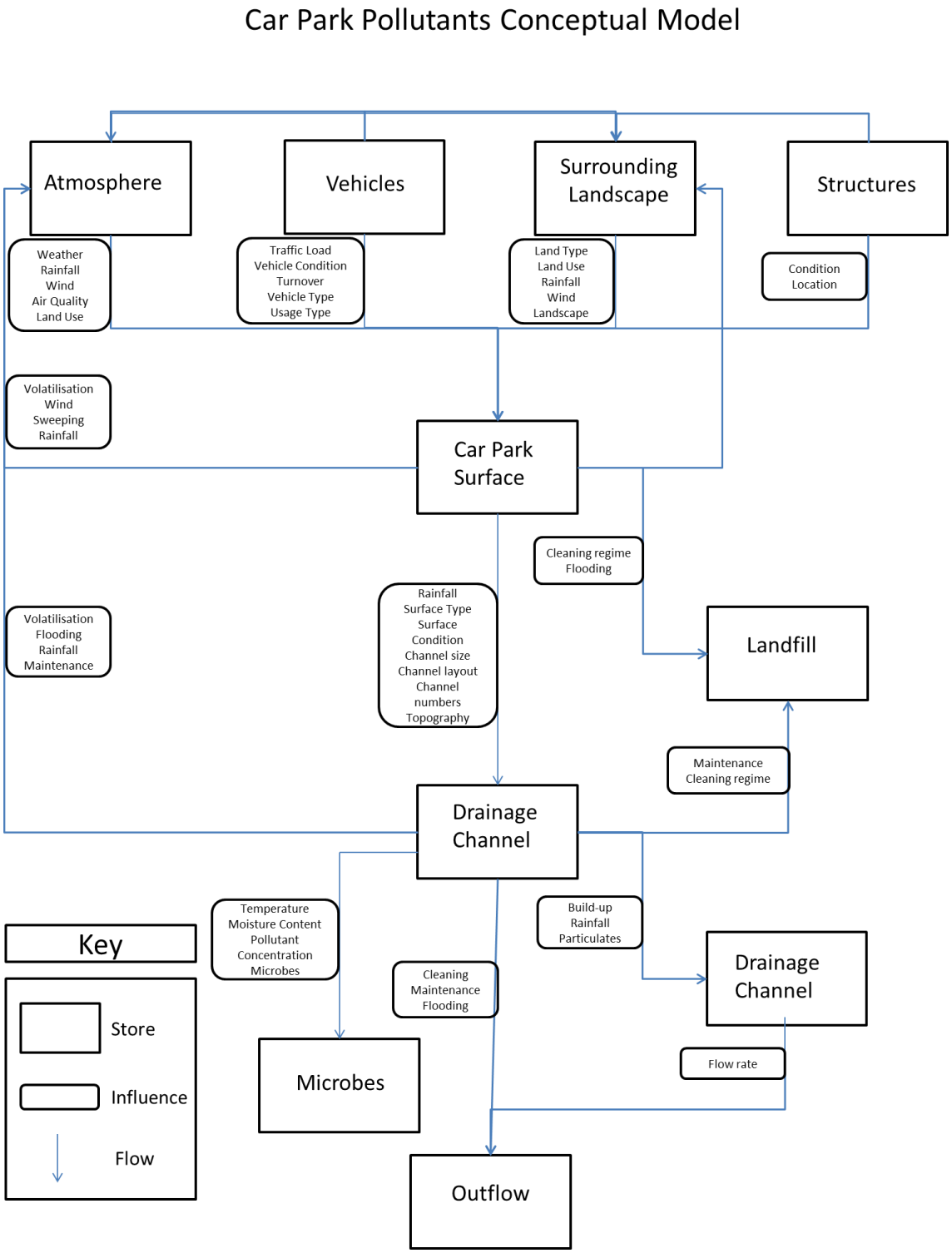

Figure 2.2: Conceptual Model of Car Park Pollutant Systems

3 Characterisation of the Physical and Chemical Properties of Car Park Surface Build-up

This paper is prepared in the format for submission to The Science of the Total Environment journal.

Within the Conceptual Model detailed in Chapter 1, this chapter addresses the 'Accumulation phase of the model. The Literature Review in the previous chapter addressed the 'Source' phase of the model, identifying the potential sources of urban pollutants, and the factors affecting them. This investigation builds on those findings, specifically focusing on characterising the pollutants accumulated on car parks.

Source → Accumulation → Transport → Treatment

The objective of this paper is to: 'Characterise the chemical and physical properties of car park surface build-up'.

3.1 Introduction

Urban pollutants are highly relevant to both human and environmental health. This is reflected in the multitude of studies focusing on the area (Robertson et al., 2003; Carraz et al., 2003; Sorme, 2003; Thorpe and Harrison, 2008; Gunawardana et al., 2012; Wei and Yang, 2012), and also legislation such as the EU Water Framework Directive (EC, 2000).

Two of the main categories of urban pollutants are heavy metals and polycyclic aromatic hydrocarbons (PAH). PAH are identified as a priority pollutant under the EU Water Framework Directive, as are some metals. Additionally, heavy metals as a whole have been identified as an environmental problem (Fu and Wang, 2011), and are known to be toxic to flora and fauna (Borchardt and Sperling, 1997; Walker et al., 1999).

Several of the predominant urban pollutants are the heavy metals: copper, nickel, lead, cadmium, zinc and chromium (Sorme, 2003; Westerlund, 2005;

Thorpe and Harrison, 2008; Ellis and Revitt, 2008). There is an abundance of potential sources for these metals to enter the natural environment, which can be grouped as vehicular and non-vehicular (Thorpe and Harrison, 2008; Sorme, 2003). Non-vehicular sources come from a range of manufactured goods, such as copper from cables and long life goods, nickel and chromium from stainless steel, lead from paints and cable sheathing, cadmium from use as a stabiliser in PVC goods and zinc from galvanised items.

It has been observed that the metal particles are adsorbed by sediment particles (Vaze and Chiew, 2004; Bjorkland, 2011), deposited from sources such as surrounding planted areas. Several studies have been carried out in order to investigate the physical and chemical properties of highway sediment, or road dust, such as Robertson et al. (2003), Gunawardana et al. (2012) and Wei and Yang (2012). Car parks are mentioned in two of these studies, however, they are the not subject of investigation. For example, Bris et al. (1999) used a car park for convenience of methodology trials, and Vaze and Chiew (2002) use parking spaces situated on highways. Despite this, the importance of car parks as sources of pollution is starting to be realised. For example, Davis et al. (2010) identified that up to 6.57 % of land take in urban areas is car parks, which is a potential for build-up of pollutants. Additionally, the draft National Standards for SUDS (2015) will potentially require a ratio of green drainage systems to pave area of 4:1, suggesting an importance.

The potential for differences between car park and highway road dusts lies in the factors identified as influences. These include, annual average daily traffic (AADT), land use, and time for which vehicles are resident. Of these, AADT is the most important, as a highway may have thousands of vehicles passing per day, whereas a car park may have as low as ten. However, despite lower numbers, the length of time vehicles reside is greater, for example, typically 8 hours in an office environment. Furthermore, vehicles are generally required to manoeuvre more in order to enter parking. Tyre and brake wear has been identified as major source of pollutants (Thorpe and Harrison, 2008; Sorme, 2003), so this may have a greater effect.

The objective of this study was to determine whether the physical and chemical characteristics of car park surface sediment are similar those of highways. Another objective was to compare the characteristics of sediment from different usage types and also different geographical locations, to see if these factors had an effect.

To achieve this, car park sediment was sampled using a ‘wet vac method, and analysed for particle size distribution, heavy metal concentration, and PAH concentration. Once these results were obtained, statistical analysis was used to determine whether car parks with different characteristics, in particular usage type, presented significantly different values. Additionally, the correlation between particle size and metal concentration was analysed. Finally, the study sought to determine whether the particle size distribution and metal concentrations in the car park sediment were similar to those found on highways.

3.2 Methodology

3.2.1 Sample Sites

In order to get a fair and representative sample, taking into account locational and usage variables and anomalies, such as isolated spills, 14 car parks were sampled (Table 3.1). The sites chosen were predominantly commercial sites (supermarkets), as these are where channel drains are widely used. Sites with other uses – office and industrial use – were also included in order to compare results to determine whether usage affected characteristics of the sediment build-up.

The site locations were also split into two geographical areas, the South East (around Milton Keynes and Bedford) and the Midlands (around Birmingham and the surrounding areas), in order to observe any potential variation due to geography/climate on the results, such as rainfall or the presence of industry.

Table 3.1: Car Park Sampling Locations

Car Park	Usage Type	Location
A	Commercial	South East
B	Commercial	South East
C	Commercial	South East
D	Commercial	South East
E	Commericial *	South East
F	Commercial	Midlands
G	Commercial	Midlands
H	Commercial	Midlands
I	Commercial	Midlands
J	Office	South East
K	Office	South East
L	Industrial/Office	South East
M	Office	South East
N	Supermarket	South East

* Underground/Covered Car Park

Car parks usage has been split into three different types, as follows:

- Commercial: Supermarkets, or other shopping facilities, where typical stay is no more than 2 – 3 hours.
- Office: Places of work, where typical stay is around 8 hours, and there is no industrial activity.
- Industrial: Where typical stay is around 8 hours, but there is industrial activity, such as heavy plant present.

All of the car parks were asphalt, with the exception of site D, which featured block paving. All of the car parks were relatively flat, with small amounts of surrounding earth and vegetation. AADT of the car parks was not measured, but it was observed during sampling that the usage pattern was generally as described above.

Samples were taken in triplicate at 5 parking spaces on each car park. The bays were chosen by allocating a number to each one, and using a random number generator to choose those to be sampled.

For each car park, the recent history was established with the proprietors regarding: sweeping regime, spills, tipping, age of car park and any recent construction activity. This was done in order to account for any possible reasons for variation in results, as these were identified as potential variables.

3.2.2 Sample Collection

Although there is a lack of studies on the contents of pollutant loadings on car parks, several have undertaken similar investigations on highway surfaces. From these, the most common method (Bris et al., 1999; Vaze and Chiew, 2002; Deletic and Orr, 2005; Herngren et al., 2006; Kayhanian et al., 2007) appears to be the use of a vacuum cleaner in order to collect the sediment.

Two main variations can be determined, the first of which being the ‘wet’ or ‘dry’ method. The wet method (Bris et al., 1999; Deletic and Orr, 2005) involves the application of deionised water at a suitable pressure in order to dislodge particles, which are then simultaneously vacuumed up. On the other hand, the dry method involves the disturbance of particles by physical methods, such as sweeping with a stiff brush prior to vacuuming (Ball et al., 1998), scrubbed with a fibre brush (Vaze and Chiew, 2002) or scrubbed with a brush four times (Herngren et al., 2006).

The second variation present in the previous investigations is the capture method via the vacuum. Whilst most of the studies simply involve vacuuming the particles straight up into the device, (Bris et al., 1999) includes an interceptor. This takes the form of a 34 L capacity plastic container filled partially with water, in order to act as a hydrolon, trapping particles of a smaller size. Kayhanian et al. (2012) used a modern vacuum with a HEPA filter, to capture particles from 0.3 µm in diameter.

The method used in this study was the wet method, using a 5L garden pesticide sprayer (Deletic and Orr, 2005), as it has been deemed to be more effective in particle mobilisation than sweeping. One litre of water was sprayed at a pressure of 300 kPa over a pre marked 0.5 m^2 area. A portable vacuum cleaner (DeWalt dc501) with HEPA filter was then used to capture the pollutants mobilised by the water (Kayhanian et al., 2012). This method was chosen due to advances in technology meaning that additions such as an interceptor were not necessary. This reduces the stages in capture, and thus lessens the possibility for error. The process can be seen in Figure 3.1.

(a)

(b)

Figure 3.1: (a) Wet Vac Sampling Setup; (b) Wet Vac Sampling Process

3.2.3 Analytical Methods

The following analytical methods were used in the analysis of the samples. Comprehensive descriptions of these methods are detailed in *Appendix A.*

3.2.3.1 Particle Size Distribution

A MasterSizer 2000 (Malvern Instruments, Malvern, Worcestershire) was used to measure the particle size distribution. This is done by the Fraunhofer diffraction theory, and light scattered from the sample is measured on a series of detectors. Where possible, analysis took place on the day of collection to prevent agglomeration of particles. In the instance this was not possible, the samples were shaken daily until analysis could be completed.

3.2.3.2 Heavy Metal Concentration

In order to analyse the metal content of the samples, they were first finely ground and 0.5g digested with aqua regia (2 ml HNO_3, 6 ml HCL) in a Perkin Elmer microwave system. Copper, nickel, lead, cadmium, zinc and chromium concentrations were then determined using an atomic absorption spectrophotometer (AAnlayst 800, PerkinElmer Ltd, Waltham, Massachusetts).

3.2.3.3 PAH

PAH Analysis was carried out via GC-MS by a professional laboratory, Alcontrol Laboratories (Hawarden, Flintshire).

3.3 Results

3.3.1 Particle Size Distribution

The graphs in Figure 3.2 below show examples of the varying particle size distributions. Some sites show unimodal distributions, with one clear peak,

whereas others show a bi modal distribution, with a second peak. It is quite noticeable that in the majority of cases, the first peak of those with a bimodal distribution corresponds to the peak of the unimodal distributions at around 80-100 µm.

In order to compare the PSD of the samples, the d50 value was used; this is to say the median value, at which half the volume of measured values fall below. By using this value, the characteristics of the sediment can be examined. This method is used Poleto at al. (2009) to assess the classification of the sediment using the d50 value as a point of comparison.

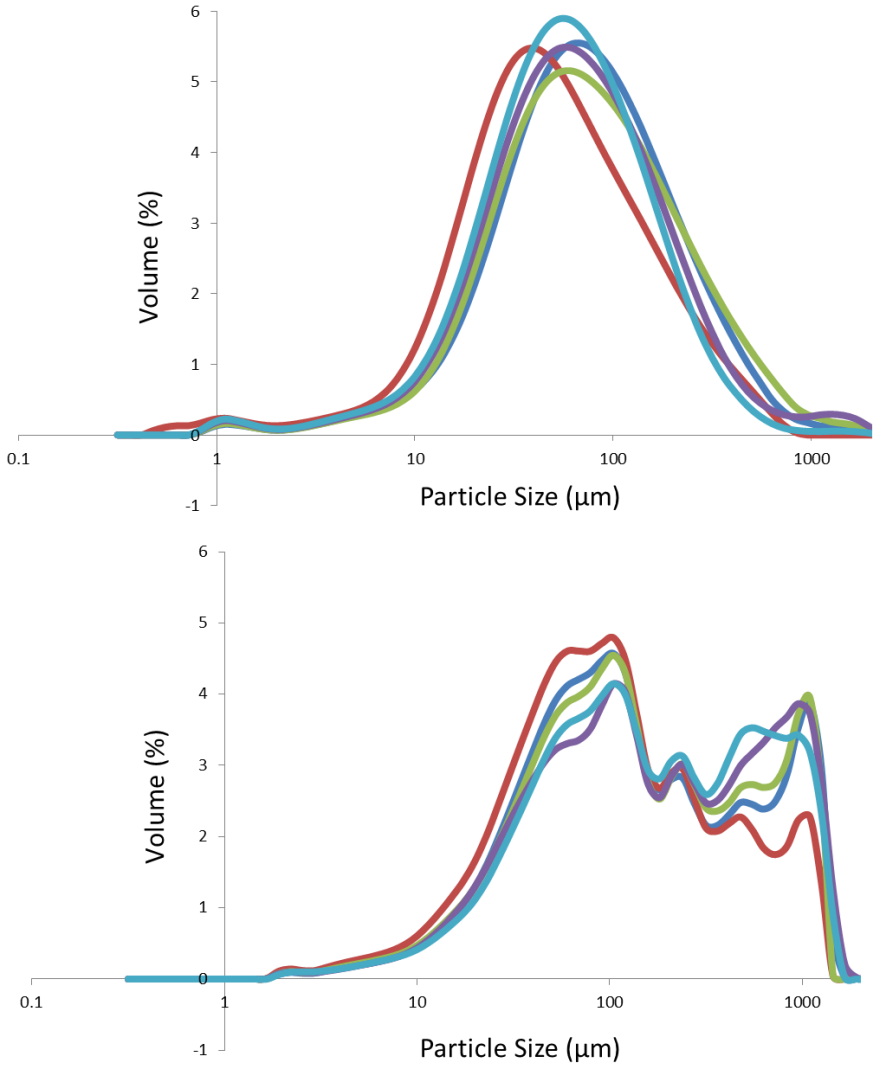

Figure 3.2: Examples of Particle Size Distributions Observed in Samples

Table 3.2: Particle Size Characteristics of Samples

Location	d50 (µm)	% Volume Between					
		0.1µm-63.00µm	63.01µm-125.00µm	125.01µm-250.00µm	250.01µm-500.00µm	500.01µm-1000.00µm	1000.01µm-2000.00µm
	77.77	43.15	24.57	15.16	7.70	5.96	3.44
	71.60	45.31	25.76	16.36	12.48	0.09	0.00
A	82.05	41.49	25.22	15.50	7.80	6.57	3.41
	78.59	42.50	25.13	15.81	7.41	5.43	3.70
	127.41	28.08	21.39	19.24	15.76	10.85	4.68
	84.43	39.99	24.25	19.88	7.93	7.65	0.29
	123.20	29.60	20.81	21.64	17.40	9.24	1.32
B	101.88	33.02	24.59	21.58	11.59	7.44	1.76
	106.14	32.63	22.64	19.73	14.00	9.10	1.88
	123.06	28.59	21.93	24.55	14.95	9.20	0.76
	84.00	39.33	24.02	19.51	8.20	6.36	2.58
	78.35	40.44	29.51	26.12	3.92	0.00	0.00
C	78.07	42.36	26.37	18.93	11.22	1.11	0.00
	101.00	32.60	24.24	21.86	17.95	3.34	0.00
	99.51	30.36	27.19	23.11	15.04	4.29	0.00
	62.31	50.39	26.34	20.59	2.67	0.00	0.00
	68.46	46.86	27.28	23.83	2.03	0.00	0.00
D	93.04	36.12	23.08	23.74	13.89	3.17	0.00
	63.17	49.89	32.91	15.75	1.44	0.00	0.00
	78.76	41.28	26.43	19.72	9.77	2.80	0.00
	71.99	44.70	27.27	17.23	8.64	2.15	0.00
	71.86	44.96	30.00	22.30	2.73	0.00	0.00
E	73.16	43.69	29.48	24.22	2.61	0.00	0.00
	74.05	42.97	30.19	24.27	2.56	0.00	0.00
	79.20	40.72	27.82	21.19	8.08	2.18	0.00
	70.94	46.33	21.54	15.75	9.28	5.12	1.98
	71.32	46.08	23.19	16.83	7.38	4.29	2.23
F	103.21	34.58	22.17	20.20	16.09	6.12	0.83
	85.64	40.43	22.51	18.19	11.97	5.81	1.09
	92.15	36.89	24.60	18.12	11.45	6.47	2.46
	65.35	48.81	23.18	15.10	6.72	3.90	2.29
	62.67	50.19	24.69	12.79	3.68	4.75	3.89
G	69.87	46.81	21.47	14.18	6.41	6.39	4.73
	106.49	35.58	19.13	16.29	12.05	11.63	5.32
	77.93	44.79	16.51	11.59	8.78	11.09	7.24
	131.62	27.79	20.53	21.43	14.48	9.66	6.10
	112.54	31.60	22.38	21.79	9.55	7.89	6.78
H	110.50	33.40	20.80	20.23	11.52	9.21	4.83
	94.05	38.03	22.74	18.37	6.52	7.48	6.85
	71.60	46.75	19.56	14.35	5.87	7.48	5.99
	98.82	37.83	19.90	18.02	10.24	8.04	5.97
	127.00	27.88	21.53	23.08	10.87	8.76	7.87
I	79.47	43.63	21.30	17.22	6.22	5.82	5.80
	100.24	34.77	23.82	17.79	4.74	9.35	9.54
	107.70	34.21	21.12	18.15	6.75	9.70	10.07
	103.20	-	-	-	-	-	-
	104.69	-	-	-	-	-	-
J	69.15	-	-	-	-	-	-
	82.87	-	-	-	-	-	-
	65.43	-	-	-	-	-	-
	39.33	-	-	-	-	-	-
	72.67	-	-	-	-	-	-
K	64.95	-	-	-	-	-	-
	44.16	-	-	-	-	-	-
	79.64	-	-	-	-	-	-
	67.40	-	-	-	-	-	-
	54.98	-	-	-	-	-	-
L	64.04	-	-	-	-	-	-
	61.58	-	-	-	-	-	-
	52.44	-	-	-	-	-	-
	60.86	-	-	-	-	-	-
	68.08	-	-	-	-	-	-
M	92.88	-	-	-	-	-	-
	104.41	-	-	-	-	-	-
	92.24	-	-	-	-	-	-
	90.94	-	-	-	-	-	-
	98.34	-	-	-	-	-	-
N	119.07	-	-	-	-	-	-
	121.92	-	-	-	-	-	-
	143.51	-	-	-	-	-	-

*** - Indicates a separate phase of sampling whereby it was not possible to split the results into size bandings.**

As Table 3.2 and Figure 3.3 show, the d50 values varied, both within and among sites. An ANOVA test showed significant difference between the sites

(p = 0.0000). A Fishers Least Significant Difference (LSD) test was then applied to the data, the results of which are displayed in Figure 3.4. This showed that several groups of sites were not significantly different from each other, indicated by the same letter in the 'Groups' column in Figure 4.4. No patterns in either usage type or geographical locations were identified within the groups shown to have no significant difference.

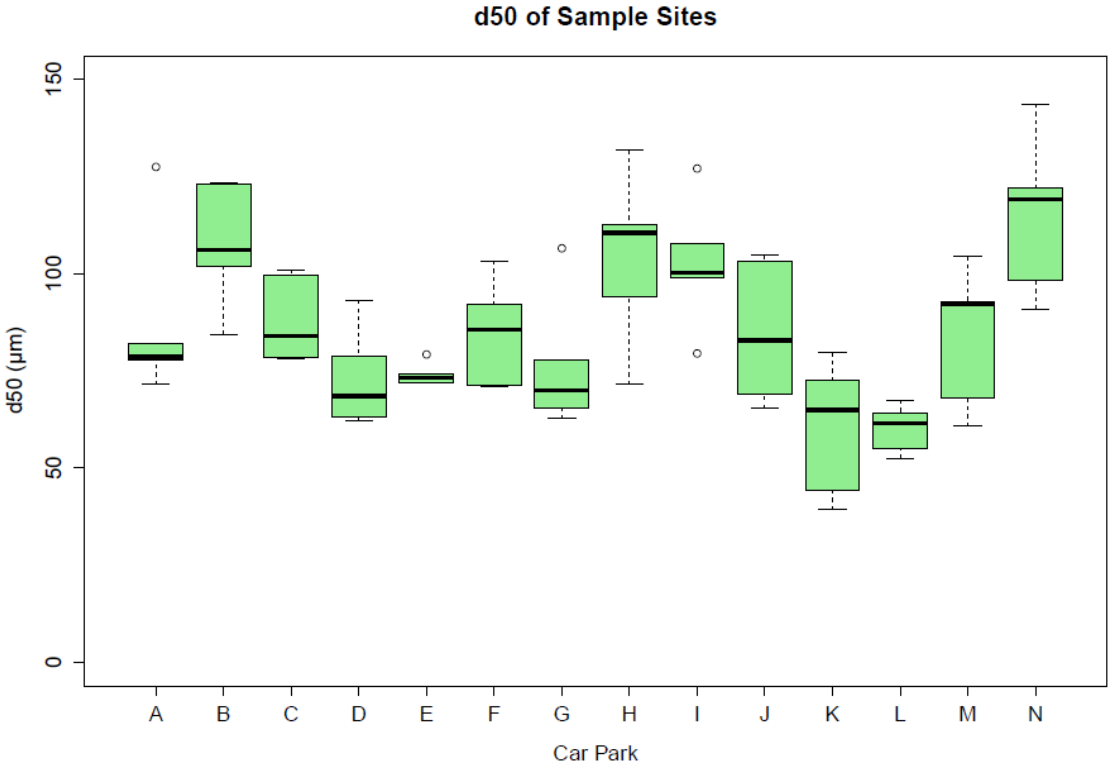

Figure 3.3: d50 Values of Samples by Site

```
Means with the same letter are not significantly
different.


Groups, Treatments and means

a     N    114.8

ab    B    107.7

abc   H    104.1

abc   I    102.6

bcd   C    88.19

bcd   A    87.48

cd    J    85.07

cd    F    84.65

cd    M    83.69

de    G    76.46

de    E    74.05

de    D    73.15

e     K    60.15

e     L    60.09
```

Figure 3.4 Fishers LSD Test Output for d50 Values

3.3.2 Heavy Metals

The results of the heavy metal analysis are shown in Table 4.3 and Figure 3.5. A wide range of values were obtained, therefore ANOVA tests were applied to each of the 6 metals, with only Ni showing no significant difference between Car Parks ($p = 0.134$). Cd, Cu, Cr, Pb and Zn were deemed to be significantly different, and as such, a LSD test was then applied. Due to the numerous

metals/locations, a summary of the results of the LSD Test are summarised in Table 3.4, with groups with the same letter showing no significant difference. The full output from the ANOVA and LSD Tests can be found in Appendix A.1 and A.2 respectively.

Table 3.3: Metal Concentrations of Samples

Site	Metal Concentration					
	Cd (µg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
	533.93	70.06	209.58	50.90	41.52	927.12
	456.78	66.43	175.27	47.62	20.61	841.93
A	152.97	70.99	187.36	48.19	21.40	807.12
	413.01	65.07	161.36	46.85	16.62	685.16
	420.84	64.68	209.42	52.90	18.37	656.40
	736.08	74.87	261.13	58.10	49.31	1100.22
	803.12	68.69	220.45	59.11	43.53	1294.33
B	741.94	70.27	204.40	63.86	36.84	965.17
	901.44	83.73	214.14	61.10	106.77	1007.41
	687.00	64.20	191.40	70.60	40.60	844.20
	597.88	56.30	174.91	49.29	20.64	662.59
	509.71	56.26	201.00	46.65	9.01	750.75
C	559.62	62.63	211.08	47.82	30.61	865.35
	412.25	54.23	200.52	46.03	-3.80	697.82
	20.24	57.50	185.53	44.48	18.43	683.83
	1222.84	53.12	197.28	51.12	39.94	927.12
	1234.81	44.36	165.87	44.96	31.77	841.93
D	1243.65	42.17	145.71	42.97	30.58	807.12
	1043.13	50.60	184.01	50.32	9.78	685.16
	1151.23	44.41	178.47	51.23	7.90	656.40
	25.25	47.49	221.44	36.07	8.02	1566.73
	817.60	50.00	301.60	37.60	6.40	1604.00
E	775.60	54.40	287.00	36.20	*	1693.60
	33.95	58.32	299.58	36.75	*	1644.50
	926.91	60.87	290.55	36.64	3.00	1868.64
	1177.15	63.13	202.00	30.66	172.55	791.18
	1122.60	68.51	197.52	43.47	77.12	873.60
F	1355.03	65.30	206.67	43.93	79.07	919.93
	972.17	59.07	190.03	58.07	65.68	810.97
	872.15	64.52	179.78	45.15	60.93	745.31
	879.40	60.60	208.80	49.60	42.00	851.40
	725.67	69.33	228.97	53.95	33.37	720.48
G	670.46	73.45	237.92	50.90	34.53	730.14
	728.06	73.15	225.65	55.31	33.87	674.95
	385.14	202.70	256.76	432.43	*	479.73
	1304.61	53.31	212.22	45.29	78.76	717.03
	1524.66	55.50	236.77	46.92	75.06	851.07
H	1691.31	57.14	227.77	44.36	73.53	929.67
	1762.93	58.12	236.47	53.71	108.22	1214.83
	1754.64	54.70	233.78	45.12	83.85	1095.63
	1376.05	52.18	218.11	44.38	63.37	1005.40
	926.93	62.06	221.82	46.85	46.45	904.10
I	1119.91	65.74	233.82	51.48	45.07	974.16
	833.90	65.96	239.66	53.97	56.57	904.46
	1118.63	57.34	222.32	57.56	39.76	999.12
	377.73	55.01	98.96	25.64	82.84	274.51
	398.84	42.97	91.07	13.79	85.27	260.47
J	367.68	51.03	88.68	28.51	76.49	233.53
	386.73	45.17	101.87	28.65	78.75	351.24
	519.70	46.31	104.21	31.91	82.35	469.55
	319.57	54.13	127.30	37.39	91.57	283.57
	424.78	55.43	88.63	24.53	92.43	345.14
K	411.29	82.86	87.19	41.10	96.59	370.47
	188.20	59.52	171.99	51.66	78.33	268.46
	277.19	35.61	79.04	28.15	77.16	253.50
	494.61	43.62	109.58	35.55	137.96	242.81
	311.71	35.11	65.42	36.04	98.53	291.66
L	246.70	31.27	67.34	28.54	74.74	255.54
	268.44	40.35	74.23	31.48	71.24	161.88
	309.54	50.11	97.49	35.99	113.95	286.36
	431.65	62.28	60.17	31.38	161.70	405.14
	324.10	68.88	62.69	27.84	231.50	308.90
M	533.27	84.10	72.50	27.61	241.30	506.63
	484.34	118.13	62.46	43.68	334.77	390.46
	325.27	73.89	66.49	29.90	236.48	462.47
	113.12	16.07	36.21	17.21	66.37	168.96
	121.87	25.78	61.23	29.39	67.84	182.96
N	129.50	26.42	54.42	24.07	47.20	163.25
	229.70	18.66	70.94	35.12	64.71	494.32
	95.10	49.93	110.18	29.51	175.51	251.66

*Concentration was below LOD

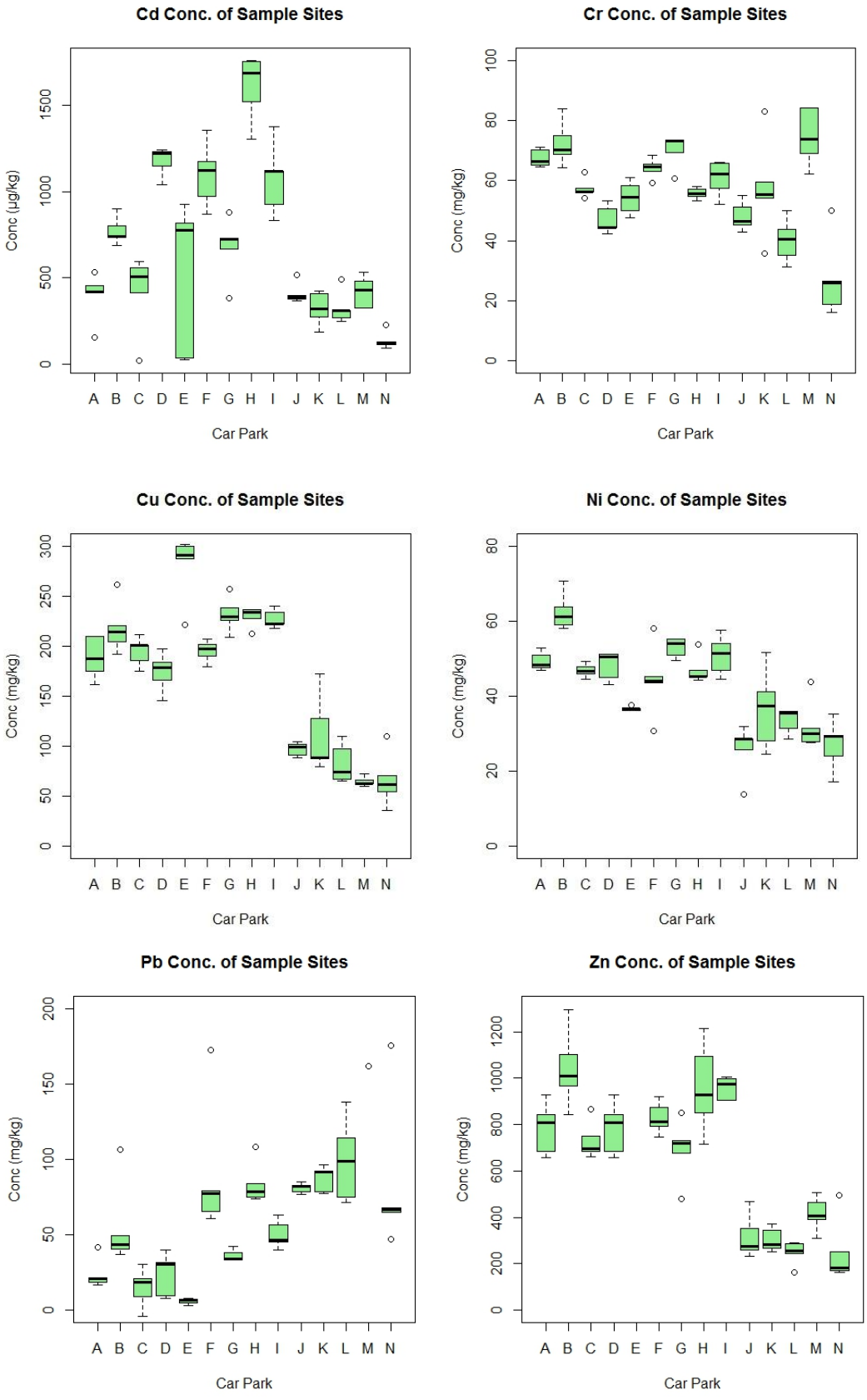

Figure 3.5: Metal Concentrations of Samples by Site

Table 3.4: Fishers LSD Test Summary for Metal Concentrations

	Metal					
Site	Cd	Cr	Cu	Ni	Pb	Zn
A	e	bcd	d	b	efg	d
B	cd	bc	bc	b	cde	b
C	e	cde	cd	b	fg	d
D	b	def	d	b	efg	d
E	de	cde	a	b	g	a
F	b	bcd	cd	b	bc	cd
G	cd	a	b	a	efg	d
H	a	cde	b	b	bcd	bc
I	b	bcde	b	b	def	bc
J	e	def	ef	b	bcd	ef
K	ef	cde	e	b	bc	ef
L	ef	ef	fg	b	b	f
M	e	ab	g	b	a	ef
N	f	f	g	b	bcd	f

Table 3.4 shows that there is much overlap between sites, with most car parks showing no significant difference with at least one other, and in the majority of cases, several. This is not surprising, given the amount of variance within the samples (S.D. = 23.5 – 441.5).

The results show a considerable amount of variation, both within and between car parks. Concentrations of the metals ranged from: Cd 20.24 – 1762.93 µg/kg, Cu 16.07 – 202.70 mg/kg, Cr 36.21 – 301.60 mg/kg, Ni 13.79 – 432.43 mg/kg, Pb 0 – 334.77 mg/kg, and Zn 161.88 – 1868.64 mg/kg. No car park showed consistently higher or lower values than others, with the exception of Pb on site E identified as being contaminated by lead paint.

3.3.3 PAH

The results of the Total PAH analysis are shown in Table 3.5: and Figure 3.6. Only sites A -I (from one phase of sampling) were analysed for Total PAH due to budgetary constraints.

Table 3.5: TPAH Concentrations of Samples

Site	TPAH (µg/kg)
A	5450
	5790
	8140
	*
	5550
B	9130
	*
	5010
	3040
	7120
C	4200
	2670
	1710
	1180
	*
D	*
	*
	1690
	*
	*
E	7680
	*
	5940
	10300
	5040
F	2030
	*
	4780
	3890
	598
G	3300
	1750
	1730
	*
	*
H	1560
	*
	3870
	1940
	2850
I	*
	*
	*
	*
	*

* Concentration was below LOD

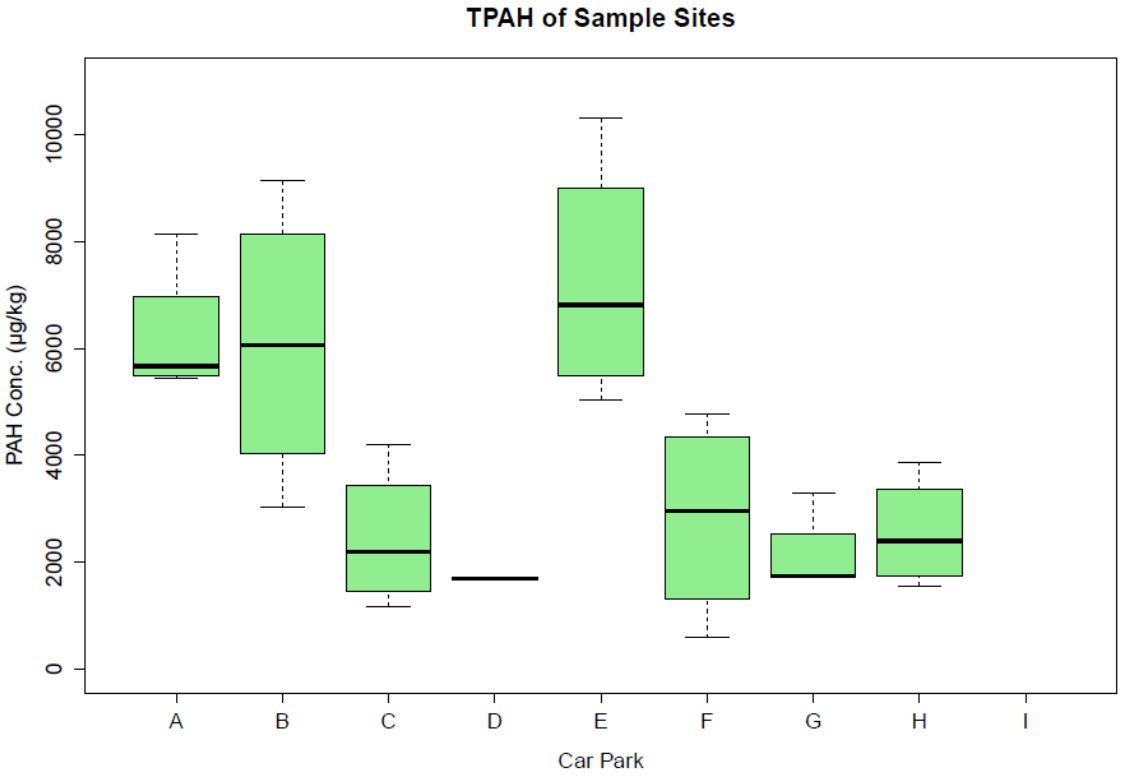

Figure 3.6: TPAH Concentration of Samples by Site

A key observation is the large number of samples with concentrations below the limit of detection (LOD), shown by '*' in Table 3.5. None of the samples from Site I had detectable concentrations of PAH, with each of the other sites ranging from 1 – 5 values below the LOD.

Those with concentrations above the LOD are plotted in Figure 3.6. The plot shows that the concentrations vary considerably (S.D. = 2,897.16), from concentrations just above LOD to 10,300 µg/kg. An ANOVA test showed that there was significant difference between the samples ($p = 0.0015$). A subsequent LSD test showed that Car Parks A, B and E were not significantly different from each other, likewise C, D, G, G and H. This can be seen in Figure 3.6, with the overlap between sets of 'boxes', and through the results of the LSD Test in Figure 3.7 below.

```
Means with the same letter are not significantly different.


Groups, Treatments and means
a       E       7240
a       A       6232
a       B       6075
b       F       2824
b       H       2555
b       C       2440
b       G       2260
b       D       1690
```

Figure 3.7: Fishers LSD Test Output for TPAH Concentration

3.3.3.1 Correlation

The correlation coefficients for metal concentration and d50 values were calculated, and are shown in Table 3.6. None of the metals showed more than 'very weak' correlation (Evans, 1996), with Ni showing a slightly negative correlation.

Table 3.6: Correlation Coefficients of Metals and d50

Metal	Correlation Coefficient
Cd	0.1425
Cr	0.0011
Cu	0.0863
Ni	-0.0039
Pb	0.0403
Zn	0.0765

Similarly, the correlation coefficient between the d50 value and PAH concentration was calculated. Displayed in Table 4.7, it can be seen that with a coefficient of -0.05789, there is a lack of correlation.

Table 3.7: Correlation Coefficients of TPAH and d50

	d50	*pah*
d50	1	
pah	-0.05789	1

3.4 Discussion

3.4.1 Car Park Observations

As described in the Methodology section, a recent history of each site was researched in order to determine factors such as spillages or sweeping activities that may have affected results. No such sweeping regimes were known, likewise spills or recent construction activity. The only issue flagged was on site M, where there was potentially contamination by lead and associated metals from a historical paint spillage. It was not known exactly when the

spillage occurred, nor was the paint comprehensively cleaned up, as flecks were observed in the collected samples.

3.4.2 D50

d50 values ranged from 39 – 144 µm for the spaces in this study. These results are similar to those attained by Poleto et al. (2009), who reported a range of 26 – 122 µm in urban street dusts. Additionally, the results can be compared to Deletic and Orr (2005), who provided d50 values at 4 positions along the width of a highway. The values obtained in this study are comparable with those 2.85 m and 4.45 m from the kerb (86-107 and 106-164 µm respectively), but were considerable smaller than those 1m from the kerb (270 - 511 and 194 – 369 µm for 0 and 0.75 m distances from the kerb. However, the latter may be explained by the effect of the kerb providing a buffer for mobile particles, allowing them to be essentially captured, whereas the car parks sampled were observed not to be enclosed in this way.

Poleto et al. (2009) also examined the modal particle size in the distribution, citing a generally bi-modal distribution with first and second peaks around 80 and 300 µm respectively. The results of this study showed a combination of unimodal and bimodal distributions. The average modal particle size corresponded with the first of those found by Poleto et al. (2009), with an average value of 89 µm. Furthermore, the first peaks of those with bimodal distributions correspond approximately with these values. This suggests that that the second peaks (300 µm+) were caused by a few large particles, as a result of the bias of the Mastersizer, recording volume rather than number of particles.

Although these studies were not focused on car parks, they are the closest reference in terms of use. After comparing the results obtained in this study with those mentioned, it can be concluded that in terms of particle size, car parks and highways give results within the same ranges.

The d50 values obtained were also compared to each other in order to examine the variation between sample sites. Results of the LSD Test showed overlap between car parks, for example, 8 out of 14 car parks showed no significant difference between one another. Although this is not all of them, given the number of sources of sediment deposition, it can be quite reasonably concluded that there is no great variation between sites.

Of particular interest was the comparison between sites of differing usage. When analysed, the results showed that this had an insignificant effect on the particle size distribution, with regards to d50 values and modal particle size. For example, Site N and Site J (commercial and office usage) were shown to be not significantly different, as were Site 3 and Site 1 (industrial and office uses). Combined with the results fitting into the ranges reported by Poleto et al. (2009) and Deletic and Orr (2005), it can be concluded usages do not have a great effect on variation.

3.4.3 Heavy Metal Concentrations

The analysis showed that of the metals analysed, Zn showed the highest concentrations. Within the urban environment, there are many potential sources of Zn, the main ones being galvanised goods such as roofs and street furniture (Sorme, 2003; CIRIA, 2007; Lundy et al., 2012). However, in the car parks sampled, neither of these were present in the nearby vicinity. It can therefore be assumed that the predominant sources of Zinc in the samples were car brakes, brake dust and tyres, which have been found to potentially contribute up to 188,000, 27,300, and 10,000 mg/kg Zn respectively (Thorpe and Harrison, 2008).

Copper and lead generally displayed the highest concentrations behind zinc. Once again, this would be expected, as they are present in brake linings, brake dust and car treads, with amounts up 234,000 (Copper) and 119,000 mg/kg (Lead) potentially contributed by brake linings and dust (Thorpe and Harrison, 2008). Chromium levels found in the samples were generally slightly lower than

copper and lead. This is slightly more surprising, as concentrations as low as 10 mg/kg have been found to be generated by brake and tyre wear, with upper values reaching 1320 mg/kg (Thorpe and Harrison, 2008). With these values around 100 times lower than maximum copper levels, proportionately, chromium concentrations in this study were relatively high.

Nickel and cadmium displayed much lower concentrations, which would be expected based on values of potential contributory sources found in studies such as Sorme (2003) and Thorpe and Harrison (2008). They report values ranging from 3.6 - 360 and 1 - 41 mg/kg for nickel and cadmium respectively, for potential contributions from brakes and tyres. The lower concentrations of these metals in the samples relate to these diminished contributors

Despite a lack of studies regarding car park pollutants, several have been carried out relating to highways. Although car parks and highways share a general usage by vehicles, it was unknown as to whether values would be similar. One of the key objectives of this study was to determine whether car parks were in fact comparable to highways in terms of heavy metal levels. Table 3.8 compares the range of metal concentrations determined in this study, along with ranges found in other literature regarding highways for comparison.

Table 3.8: Comparison of Metal Concentrations Obtained with Existing Highway Studies (mg/kg)

Metal	Conc. Range This Study	Gunawardana et al. (2012)	Wei and Yang (2012)	Robertson et al. (2003)	Carraz et al. (2003)
Copper	36-301	98.4	94.9-196.8	39-133	17-342
Nickel	13-70.6	7.01	23-86.26		
Lead	0*-334	29.1	53.3-408.41	25-260	45-1461
Cadmium	0.2-1.7	0.35	1.17-3.77		
Zinc	161-1868	236.5	1214.5-1450	122-2183	65-990
Chromium	16-202**	9.37	23.1-194.7		

* Due to calibration curve of analytical method, lower concentrations can give results around 0/ negative concentrations.

** Potential anomaly, second highest value 118.13 mg/kg.

The values for each metal obtained fit within the range of the collated alternative sources, with the exception of cadmium, whose lower limit is slightly outside the lowest reported. However, this is unsurprising given the low values (< 1 µg/kg).

In the car parks investigated, levels generally fall towards the lower end of the reported values. This could be due to the influences on the build-up of pollutants, which include AADT. The load of the car parks studied ranged from around 15 – 300 spaces, with an estimated AADT of 15 – 4000, which is low compared to that of the comparable highways studies, which were in thousands. There are several potential reasons that the values obtained were similar, despite the reduced numbers. Retention time is greater on a car park, with cars parked for, in this study, up to periods longer than 9am – 5pm for the office usage type, thus there is a greater opportunity for brake dust or loose metals from other parts of vehicles to accumulate on the surface. Additionally,

car parks require more manoeuvrability than a highway, leading to greater use of tyres and brakes. Sorme (2003) and Thorpe and Harrison (2008), report that there is potentially a vast quantity of pollutant arising from the wear of these car parts. Therefore, it could be determined that despite the smaller AADT for car parks compared to highways, the retention time of cars and wear from manoeuvring effectively balances this out.

However, these findings strongly suggest that car park pollutant levels are overall similar to those of highways. Whereas there are many potential influences on build up, fitting the results into the range of several other studies should allow these to be taken into account, giving weight to the argument.

As with the particle size, results obtained were analysed to determine whether results from different car parks were significantly different. As shown in the results section, an ANOVA test showed that only Ni was not significantly different between the 14 sites. Upon further analysis, the LSD test showed overlap between the sites, with sites showing no significant difference between one other for all metals, for a maximum of 8 of the sites. Although this is not unanimous, it can be explained by the sheer number of potential sources of pollutants identified above.

Combined with the discovery that the values generally fall within the range of those obtained by similar highways based studies, it can be concluded that the difference between sites is a result of natural variation in the sources identified.

3.4.3.1 Comparison to Reference Values

In order to put the values of the metal concentrations obtained into perspective, they have been compared to Contaminated Land Exposure Assessment (CLEA) 2009 Soil Guideline Values (SGV). The SGV, and the mean value of the metals analysed and recorded in Table 3.9 below. From the CLEA SGV, the ‘Commercial’ values have been used for comparison, as it is these that the sample sites more closely identify with.

Table 3.9: Comparison of Metal Conc.to CLEA 2009 SGV

Metal	CLEA 2009 SGV (mg/kg)	Range of Analysed Conc. (mg/kg)
Cu	130	36-301
Ni	1800	13-70.6
Pb	750	0-334
Cd	230	0.2-1.7
Zn	300	161-1868
Cr	5000	16-202

It can be seen that the upper range of the metal concentrations for Cu and Zn is above the CLEA SGV, with the lower values in the range falling well within. For the other four metals, the upper value falls within the SGV. This shows that in general, car parks have relatively low levels of heavy metal pollutants when compared to what is considered safe exposure with regards to contaminated land. For the metals outside the SGV, this is likely due to the specific sources of Cu and Zn that car parks are subjected to, as identified previously.

3.4.3.2 PAH

The concentrations determined are very low values in comparison to similar studies investigating pollutants in road dusts. For example, Mostafa (2009) found a range of PAH concentrations between 27,000 and 76,000 mg/kg for residential streets, and 279,000 to 379,000 mg/kg for heavily trafficked streets. A study by Dong and Lee (2009) found lower values, ranging from 19,690 – 68,730 µg/kg on residential streets, and 53,760 – 15,464 µg/kg in heavily trafficked areas. All values with the exception of the lowest (19,690 µg/kg) were at least five times greater than the maximum value of 10,300 µg/kg found in this study.

There are a number of factors which may contribute to the low concentrations of pollutants compared to highways. The most significant of these is likely to be the number of vehicles using a highway compared to a car park. This is twofold, in that the overall number of vehicles using a car park is likely less per day, but

also the number of vehicles travelling over (for example) a specific 0.5 m^2 area will be less, as one car is parked for several hours, whereas on a highway, every car will drive over the same spot.

Another possibility is the activity of the vehicle. For example, on a car park the car engine is not in operation, save for a limited time whilst manoeuvring into a space. In contrast, vehicles are constantly functional whilst on a highway, emitting pollutants for a greater time. It could be argued that the engine activity in a car park is more concentrated, i.e. over one space instead of a whole highway. However, the overall short period of time any one specific area will be subject to engine activity mitigates this argument.

One of the objectives of the study was to investigate the potential effect of location on the pollutant levels. From these results, it is apparent that this is not a contributing factor for PAHs, as the graph shows that levels around MK/Bedford and the Birmingham area are interspersed.

The site that stands out, having both the highest average concentration and the highest value is Site D. This is interesting, as this was an underground car park. The higher values recorded may be due to factors such as the lack of direct sunlight leading to reduced photolysis of PAH, or the lower temperature meaning less volatilisation. Shelter from the wind is also likely to be a cause of this, as deposited particles are less likely to be blown away and removed from the site.

3.4.4 Correlation of Parameters

It is widely reported with urban pollutants, in particular highways, that pollutants show an association with the smaller sediment fractions, i.e. greater concentrations of pollutants are associated with higher levels of smaller particles. Although variation does occur as to below which size this becomes significant, values range from the > 63 µm - < 150 µm range. The scope of this study, it would therefore be expected that greater concentrations of metals would be present in samples with a higher proportion of the lower (0-63/63-125

μm) fractions (Dong and Lee, 2009) (Herngren et al., 2006), equating to a lower d50 value.

However, when the d50 values were analysed, and the correlation coefficients were determined, the results showed no significant correlation. Vaze and Chiew (2002) reported a general lack of correlation between particle size and metals.

One reason for this could lie in the sources of the pollutants. It has already been identified that brake dusts, brake linings and tyre wear are potentially contributors to pollutant build up, and that this could be magnified for car parks. Additionally, it has been reported that the smaller particles are more likely to be those of the metal source, rather than those originating from the surrounding land or atmospheric deposition. Despite exhibiting d50 and modal particle size values corresponding to those in the literature, the values obtained could occur due to an averaging out of smaller metal particles, and larger sand/soil particles.

The most likely reason however, is agglomeration of particles. During residence on the car park, it is possible that particles agglomerate. This would lead to ‘larger’ particles consisting of several smaller particles, therefore inheriting the combined concentrations of metals, leading to a higher concentration in the ‘larger’ particle (made up of smaller particles) than a single particle of the same size.

3.4.5 Limitations

A review of literature discovered that there is a range of ways in which particle size distribution is both measured and reported; by volume, mass and number. This study used the analysis of particle volume, due to the equipment available, which gave a level of information sufficient in this case. In order to investigate the particle size in more depth, a mass based analysis could be used, as is the case in several other studies.

Additionally, whereas using d50 values of particle size was used to suggest trends in particle size and pollutant concentrations. This could be investigated

further by sieving the dried soil into size fractions, and analysing these separately. This would, however, require a larger sample area, as for many sample sites there would have been insufficient materials for analysis in this instance.

3.5 Conclusion

The physical and chemical characteristics of car park surface build-up were shown to be similar to those of highways. Particle size, heavy metal concentration, and PAH concentration were all shown to generally fall within the range of values reported in a number of similar studies investigating highway surface build-up. As a result of these findings, the extensive literature relating to highway pollution could be used and applied to further research on car park pollutants.

The physical and chemical characteristics of car park surface sediment were shown not to vary as a result of usage type, with variation shown between and within uses. Similar trends were shown with regards to location, with variation within and between locations.

3.5.1 Further Work

One of the findings from the study was a lack of correlation between particle size (d50) and metal concentration, as reported by several other studies. Further work on the characterisation of car park sediment could involve splitting the sediment samples into different size fractions and analysing the chemical characteristics in order to examine potential correlation in more detailed.

Additionally, the particles in the sediment samples could be analysed by microscope, or high resolution camera, in order to determine the origin of the particle and subsequent pollutants.

4 Investigation of the Effect of Rainfall Intensity on Pollutants Entering a Channel Drain

This paper is prepared in the format for submission to The Science of the Total Environment journal, or alternatively a CIWEM publication.

The next phase of the Conceptual Model is the 'Transport' phase. With the sources of pollutant identified, and the properties of the accumulated sediment characterised, in the previous chapters, this paper investigates the transport of the accumulated sediment from the car park surface, into the channel drain.

Source → Accumulation → Transport → Treatment

The objective of this paper is to: 'Quantify the effect of rainfall intensity on mobilisation and transportation pollutants.'

4.1 Introduction

The importance of urban pollutants to human and environmental health is reflected by a number of studies in the area, and legislation such as the WFD (EU, 2001), in which pollutants are addressed. One of the key constituents of urban pollution are heavy metals, which are deposited form a number of sources, both vehicular and from surrounding infrastructure Sorme (2003), Westerlund (2005), Thorpe and Harrison (2008) and Gunawardana et al. (2012), and can be toxic to flora and fauna (Borchardt and Sperling, 1997; Walker et al., 1999).

Studies have shown that these heavy metals are deposited and accumulate on paved surfaces (Robertson et al., 2003; Gunawardana et al., 2012; Wei and Yang, 2010;). Many studies have been carried out to determine the typical chemical characteristics of runoff, such as Herngren (2005), Goonetilleke (2009), Egodawatta (2007) and Egodawatta (2008). However, due to climatic variations, the most important study with regards to this investigation is

Crabtree (2006), which consisted of an extended study of the runoff from a number of rainfall events in the UK.

The urban pollutants mentioned above become an environmental problem when they are removed from the car park surface. During rainfall, pollutants are mobilised by droplets falling on the surface, and then transported via the flow of collected water into a drainage system. The drainage system subsequently transports the pollutants to either a sewer system, or directly to a watercourse. In this way, pollutants are then able to affect the natural environment in the ways detailed above.

There are several characteristics of rainfall that may affect the mobilisation, including intensity, drop size and kinetic energy (Best, 1950; Rosewell, 1986; Herngren, 2005; Egodawatta, 2007; Hvitved-Jacobsen et al., 2010). The runoff coefficient of the car park may have a subsequent effect on pollutants entering the drainage system, as it may affect transportation to the drain.

Rainfall simulation is seen as a useful tool in the analysis of runoff, eliminating some of the many variables encountered when examining 'natural' runoff (Hernrgen, 2005). The method has been utilised in investigating runoff (Goonetilleke, 2009; Egodawatta, 2008). It does however require specialized equipment to be constructed in order to exact an experiment. A method was devised by Herngren 2005, and the same apparatus was used in the other studies mentioned.

The 'first flush phenomenon' can be defined as 'the relatively high concentration of pollutants in the initial phases of combined sewer flow following a storm' (Gupta, 1996). This is as a result of a build-up of pollutant over the antecedent rainfall free period, due to accumulation and a lack of wash-off. It is however, a complicated phenomenon, due in part to the number of factors affecting both build-up and wash-off, and its existence is debated by scientists (Bach et al., 2010).

Partially as a result of the first flush theory, the National Standards for SUDS (UK, 2014) as part of the FWMA (UK, 2011) require the first 5mm of rainfall to

be contained on site, and not discharged. This is to prevent influx of high concentrations of pollutants into sewers and receiving watercourses, and also to encourage retention and on site treatment. The first flush theory is important in determining whether this requirement is required from a pollutant point of view.

The objective of this study was to investigate the effect of several different intensities on the physical and chemical properties of runoff entering a channel drain. The purpose was different to similar studies (Herngren, 2005; Goonetilleke, 2009; Egodawatta, 2008), as the focus was on what was both mobilised and transported into the drain, as opposed to only what was mobilised, or the transportation characteristics. These were however, considered when explaining the findings.

To do this, a similar method to that detailed in (Herngren, 2005) was used, albeit using a field rainfall simulator normally used for soil erosion investigations. Additionally, the methodology was also adapted to suit the aim of the study. Instead of capturing the flowing runoff using a ‘trough’, an interceptor was placed into a channel drain itself, and the runoff collected from this. In this way, it was possible to examine the physical and chemical characteristics of the sediment. The liquid aspect of the runoff was not analysed, save for volume, as the focus was on the sediment entering the channel drain.

The physical and chemical properties were characterised, and variation of these characteristics due to rainfall intensity and time quantified. This was done by analysis of the particle size distribution and heavy metal concentration for each intensity, and also identifying at any variation of the profile of the characteristics over time.

Understanding typical characteristics of pollutants entering a channel drain, and the effect different factors have on them is an important step to fully understanding the pathway of urban pollutants.

4.2 Methodology

4.2.1 Rainfall Simulator Calibration and Intensity Selection

Before the actual sampling could take place, a field rainfall simulator was set up and calibrated. The rainfall simulator consisted of a scaffold frame, with a 2 x 2m footprint. An interchangeable nozzle was attached in the centre, at a height of 2.5 m. Synthetic sheets were wrapped around the side of the setup in order to prevent 'rainfall' falling on undesired areas, and to provide a degree of protection from wind.

Calibration took place by placing 5 collection buckets under the simulator, in the 1 x 1 m area to be used for sampling, as shown in Figure 4.1 below. Different combinations of pump pressure and nozzle size were then tested to obtain the desired intensities. The nozzle/pressure information and results of the calibration are detailed in *Appendix C.1.*

(a)

(b)

Figure 4.1: (a) Rainfall Simulator Calibration Setup and (b) Rainfall Simulator Calibration Process.

‘Rainfall’ was collected over a period of 15 minutes, and the volume measured at the end of the time. This was averaged across the 5 collection buckets, and multiplied by 4 to determine the intensity in mm/h. Additionally, a coefficient of variation was calculated between the buckets. This was done in order to assess the uniformity of the rainfall, and ensure there was a relatively even intensity falling across the sample area, and not just as a whole.

Initially, it was intended that a number of intensities would be selected to represent a standard range of storm events, such as 1 in 1, 10, 100, 1000 and 10,000 year events. However, it became evident during the calibration stage that it was difficult to simulate an intensity of lower than 24 mm/h due to the pressure being too low and subsequently the ‘rainfall’ became localised and lacked spread. Secondly, the variation between replicates for a single intensity was noticeable, up to 5mm/h. Therefore, it was decided to use a range of intensities whose values did not overlap during calibration process.

As a result, intensities of 24, 39, and 54 mm/h were selected. These were referenced with Flood Estimation Handbook (FEH) (CEH, 2009), and corresponded to 1 in 10, 30 and 100 year rainfall intensities respectively for a 30 minute event.

4.2.2 Sample Collection

Once the rainfall intensity settings had been determined and recorded, the sampling could begin. Spaces over 3 car parks were selected at random, in order to provide a fair representation of conditions. Due to logistical challenges, the car parks were situated on the Cranfield University Campus.

Three 200 L water butts were filled prior to sampling in order to provide the ‘rainfall’. The sample space was chosen, and the rainfall simulator set up with the nozzle in the centre of the plot. A 1 x 1 m area was bunded using lay-flat hose filled with sand, in order to contain the runoff generated from rainfall falling on the area, and prevent that from outside entering. The bund enclosed three

sides of the sample area, with the final side being the channel drain itself. The setup can be seen in Figure 4.2.

A ‘channel drain interceptor’ was placed into the channel drain prior to commencement of the rainfall. This consisted of a 1 m x 100 mm length of uPVC guttering, blocked at both ends, with rubber seal on the external edge. This, combined with the flexibility of the uPVC guttering, ensured a watertight fit into the channel.

A timer was started at the same time as the rainfall simulator, and was monitored by an assistant. Time was called every 5 minutes, at which point the contents (runoff) of the interceptor were transferred to sample collection buckets. In the event of the interceptor becoming full before the time period was up, it was removed, and replaced immediately by 1 of 3 additional interceptors. Although small sample losses may have occurred, these were minimised with careful preparation and practice.

The experiment ran for 30 minutes, after which time the remaining contents of the interceptor were collected. Samples in the collection buckets were then transferred to sample bottles for storage, and labelled with intensity, replicate and sample number.

The above process was repeated on 9 different car park spaces on 3 different car parks, with several different spaces providing replicates. Spaces within a car park were chosen as close together as possible, in order to minimise variation in conditions. Overall, each intensity replicated 3 times over the car parks. These replicates were carried out in order to obtain representative samples, and to reduce error as a result of natural variation in car park spaces. To reduce variation further, the car parks sampled shared similar characteristics. They were all constructed from the same type of asphalt, located within the university campus, and had no abnormal slope. With these actions taken, for the purpose of analysis, the spaces were treated as a single sample area, with the same intensities on different car parks. The sampling also took place concurrently, so antecedent weather conditions were the same for all.

(a)

(b)

Figure 4.2: (a) Rainfall Simulator Sampling Setup and (b) Rainfall Simulator and Channel Drain Interceptor Setup.

4.2.3 Analytical Methods

The following analytical methods were used in the analysis of the samples. Comprehensive descriptions of these methods are detailed in *Appendix A.*

4.2.3.1 Particle Size Distribution

A Malvern Instruments MasterSizer 2000 (Malvern Instruments, Malvern, Worcestershire) was used to measure the particle size distribution. This is done by the Fraunhofer diffraction theory, and light scattered from the sample is measured on a series of detectors. Where possible, analysis took place on the day of collection to prevent agglomeration of particles. In the instance this was not possible, the samples were shaken daily until analysis could be completed.

4.2.3.2 Heavy Metal Concentration

In order to analyse the metal content of the samples, they were first finely ground and 0.5g digested with aqua regia (2 ml HNO^3, 6 ml HCL) in a Perkin Elmer microwave system. Copper, nickel, lead, cadmium, zinc and chromium concentrations were then determined using an atomic absorption spectrophotometer (AAnlayst 800, Perkin Elmer Ltd, Waltham, Massachusetts).

4.3 Results

The sediment characteristics of the runoff resulting from the rainfall events in the experiment are detailed in Table 4.1 below.

Table 4.1: Mass, Volume, d50 and Metal Concentrations of Samples

Intensity (mm/h)	Time (mins)	Mass (g)	Volume (L)	d50 (µm)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cd (µg/kg)	Cr (mg/kg)
24	10	0.236	0.1	42.37	543.78	17.40	46.31	241.04	393.36	25.39
	20	0.22	0.45	78.03	514.29	16.46	43.79	227.96	372.03	24.01
	30	0.59	0.25	73.73	89.86	2.88	7.65	39.83	65.00	4.20
39	5	0.47	1.55	67.58	318.92	37.24	184.29	1742.94	945.42	80.27
	10	0.23	1.95	75.10	436.90	26.11	129.64	1338.48	775.06	57.19
	15	0.12	1.95	67.75	240.98	14.40	71.50	738.27	427.50	31.54
	20	0.37	1.8	80.34	371.05	45.48	212.95	2320.22	1699.84	93.37
	25	0.21	1.7	89.65	229.76	20.48	97.38	946.94	631.92	40.88
	30	0.29	1.5	98.57	308.86	27.54	130.91	1272.95	849.47	54.96
54	5	0.24	1	95.47	193.93	27.89	140.94	1417.00	-9.11	54.29
	10	0.12	1.3	106.75	97.41	14.01	70.79	711.77	-4.58	27.27
	15	0.15	1.3	110.34	102.52	17.68	65.02	727.46	401.11	30.53
	20	0.14	2	110.87	96.99	16.73	61.51	688.20	379.47	28.88
	25	0.10	1.2	111.36	68.10	11.74	43.18	483.20	266.43	20.28
	30	0.04	1.75	117.66	27.66	4.77	17.54	196.28	108.23	8.24
24	10	0.08	1.1	92.56	18.70	4.35	21.15	93.04	1.21	8.53
	20	0.21	0.55	92.72	49.19	11.44	55.64	244.74	3.18	22.44
	30	0.26	0.45	91.86	58.78	13.67	66.49	292.46	3.80	26.82
39	5	0.15	1.7	101.04	59.83	9.95	56.31	509.43	268.34	18.02
	10	0.35	3.9	110.70	138.16	22.98	130.03	1176.31	619.61	41.62
	15	0.44	3.9	108.06	144.89	105.56	156.19	925.63	688.52	174.05
	20	0.61	3.2	107.73	143.60	32.85	195.07	1038.65	865.81	67.29
	25	0.16	3.95	100.49	61.70	17.57	72.36	580.18	-0.39	30.24
	30	0.34	4.6	106.27	127.30	36.26	149.29	1196.99	-0.80	62.38
54	5	0.14	2.2	104.00	113.03	14.49	65.36	475.62	409.24	31.37
	10	0.21	3.8	92.32	174.38	22.35	100.83	733.78	631.36	48.39
	15	0.19	3.3	99.47	132.11	18.41	98.56	663.96	533.04	32.80
	20	0.17	2.8	95.13	116.63	16.25	87.02	586.18	470.59	28.96
	25	0.14	3	91.78	86.82	25.53	63.57	307.44	370.19	39.99
	30	0.15	1.2	92.09	93.40	27.46	68.39	330.76	398.27	43.03
24	10	0.04	0.15	128.32	17.92	4.42	16.38	68.95	159.35	5.35
	15	0.13	0.2	127.57	65.84	16.23	60.17	253.33	585.44	19.66
	20	0.10	0.3	128.63	49.79	12.27	45.50	191.56	442.68	14.87
	25	0.03	0.4	131.28	15.51	3.82	14.18	59.70	137.96	4.63
	30	0.02	0.6	145.09	7.46	1.84	6.82	28.71	66.36	2.23
39	5	0.62	2.05	146.55	136.45	82.23	128.25	562.22	1210.88	108.24
	10	0.68	2.95	136.45	151.14	41.98	138.74	611.76	1243.70	60.18
	15	0.72	3	136.70	143.03	40.41	122.42	525.11	984.00	57.01
	20	0.44	3.75	137.63	180.80	44.07	122.78	519.00	-0.22	67.91
	25	0.28	3.95	140.79	182.75	43.31	126.41	563.03	1025.00	75.70
	30	0.23	3.5	135.54	191.92	50.51	113.75	512.52	911.29	75.54
54	5	0.62	2.5	77.24	275.72	44.36	154.65	633.97	1016.38	63.74
	10	0.76	2.2	85.29	241.16	41.56	130.27	617.38	0.00	57.14
	15	0.85	2	85.24	161.90	35.78	102.54	462.52	773.94	45.97
	20	0.51	4.1	85.57	235.92	31.36	76.31	336.20	620.85	40.15
	25	0.10	4.7	86.77	273.56	118.46	57.18	294.09	789.72	140.57
	30	0.08	3	85.93	210.51	91.16	44.00	226.31	607.71	108.17

To determine the effect of rainfall intensity on the parameters, and also to look at any variation over the duration of the rainfall event, a Two-way ANOVA was applied to the data. In order to standardise the time aspect, results were taken

at 10, 20 and 30 minute intervals, using either the sum or average of values within the period where data for 5 minute intervals was obtained. The full output from the statistical tests is recorded in *Appendix B.2.*

4.3.1 Runoff Volume

The results of the ANOVA test showed that the volume of runoff did not vary with time ($p = 0.5537$), but did vary with intensity ($p = < 0.0001$). A post hoc test in the form of a Fishers Least Significant Difference Test was applied to the result, which determined that the results from the 39 and 54 mm/h intensities were not significantly different. No interaction effects between time and intensity were demonstrated ($p = 0.9344$).

4.3.2 Sediment Mass

The ANOVA test determined that the mass of sediment washed off during the rainfall event did not vary with time ($p = 0.2646$), but did vary as a result of intensity ($p = 0.0159$). This variation was shown not to be as a result of variation in runoff volume, as the correlation with sediment mass was shown to be weak (correlation coefficient = 0.27). A LSD Test was applied to the data, which showed that there was no significant difference between the results of the 24 and 39 mm/h results, and the 39 and 54 mm/h results. No interaction effects between time and intensity were shown ($p = 0.5026$).

4.3.3 Particle Size Distribution

The ANOVA showed that the d50 value did not show variation as a result of time ($p = 0.8321$), neither did it vary with intensity ($p = 0.5832$). Subsequently, no interaction effects were shown between the d50 value and time/intensity.

Given that no variation was shown in the results between the different conditions, the average d50 was calculated as 100 µm +/- 9.1 µm (S.D. 24.1 µm).

4.3.4 Heavy Metals Concentrations

The results from the analysis of heavy metals are shown in Table 4.2 below, with the outputs from the statistical test in the top half, and interpretations of results below. An ANOVA test was applied to the concentration of metals in each of the samples. Variation with intensity was shown by 5 of the 6 metals (highlighted red in Table 5.2:), and variation with time shown by Pb alone ($p = 0.0300$). Cu did not vary with either intensity or time.

Post hoc, a Fishers LSD Test was applied to the 5 metals showing variation with intensity. Of these, the 24 mm/h event was shown to give the lowest concentration in every case. In 4 of the 5 cases, the results from the 54 mm/h event were shown to be not significantly different to both the 24 mm/h event, and the 54 mm/h event, whereas for Pb, all intensities were shown to give significantly different results. No interaction effects between time and intensity were shown for any of the metals.

Table 4.2: Statistical Summary of Metal Concentrations

		Metal					
		Cu	Ni	Pb	Zn	Cd	Cr
Average		173.84	26.93	81.99	554.11	446.96	42.98
C.I		55.56	8.68	17.75	158.20	132.34	11.98
P Intensity		0.761	0.024	0.000	0.000	0.004	0.002
P Time		0.572	0.902	0.030	0.264	0.429	0.901
P (Interaction)		0.925	0.599	0.164	0.720	0.867	0.547
Group (LSD Test)	24	a	a	a	a	a	a
	39	a	b	b	b	b	b
	54	a	ab	c	ab	ab	ab

Concentrations in mg/kg, Cd µg/kg.

4.4 Discussion

The methodology for the study was based on that of Herngren (2005), which has been successfully used repeatedly. There were, however, several constraints that prevented this study following the methodology as closely as desired. The field rainfall simulator used was primarily designed for experiments on soil erosion in storm events, and as such was designed for higher rainfall intensities. The pump and nozzle method of controlling intensity means that intensities were affected by limited nozzle sizes, and pressure requirement to form an even spread.

This meant there were problems achieving the lower intensities that are more representative of storms in the UK. It may be possible to attain these intensities using specifically designed apparatus, with lower pressure requirements, or other distribution methods such as capillary tubes. This would give more options as to the range of intensities investigated.

4.4.1 D50

The lack of variation in d50 values over time or with rainfall intensity suggested that here were no particular particle sizes are preferentially washed off. It may be expected that higher intensities may mobilise larger particles, as a result of the greater kinetic energy in higher intensities providing more mobilisation, however this was not found. It is possible that this scenario would occur with larger or lower intensities than those included in this study, but the energy in the rainfall intensities in this are sufficiently similar to one another that they mobilise sediment with the same physical characteristics.

The average d50 value was 100 µm, which is similar to several studies that analysed the runoff from highways, such as Deletic and Orr (2005) and Poleto et al. (2009), which ranged from 26 - 122 µm and 86 – 369 µm respectively. Given the differing uses, and the many different sources of sediment, it is interesting that the physical characteristics of the sediment in runoff are similar for car parks and highways.

4.4.2 Runoff Volume

The volume of runoff generated from the rainfall events was shown not to vary with time. This is most likely due to the relatively shallow storage of the car park surface. As a result of this, even the lower intensity exceeds the storage capacity, and therefore there is no detectable delay or other variation exhibited.

It was shown that the runoff volume varied with intensity, with the least for the 24mm/h intensity was shown to be the lowest, as by definition involved the least amount of ‘rain’ for the duration, however no significant difference was shown between the 39 and 54 mm/h intensities. It would be expected that the higher the intensity, the greater the runoff volume. The reason for this not being displayed it likely due to the runoff coefficient of the site, a dimensionless coefficient which relates the rainfall volume, to the volume of resulting runoff. In the case of car parks, the factors affecting this include ‘pore’ spaces on the surface, allowing for storage of water, surface material, and topography of the sample space. This may be exacerbated by the small sample size.

4.4.3 Sediment Mass

The mass of sediment was shown to vary with intensity, but not time. This variation was shown not to be as a result of volume, as the correlation between volume and mass was very weak. Although it would be expected that the higher the intensity, the greater the mass, the difference between the 39 and 54 mm/h intensities was not significant.

It is suggested that the kinetic energy of the rain droplets is the reason, with higher intensities having higher kinetic energy, and thus mobilising more of the sediment build-up. The 39 and 54 mm/h intensities not being significantly different suggests that there is a threshold between 24 mm/h and 39mm/h where mobilisation changes. However, it was also shown that there was no significant difference between the results from the 24 mm/h intensity and the 54 mm/h intensity. This overlap tends to suggest that natural variation in sediment mobilisation is greater than the effect of the intensity.

Another possibility for the non-linear increase is the nature of rainfall simulation apparatus. As described in the methodology section, the intensity is a function of nozzle size and pressure. In order to achieve the desired intensities, the 39 and 54 mm/h used the same nozzle, with differing pressures (39 mm/h = 14.5 psi, 54 mm/h = 21.8 psi). It is possible that the increased pressure for the 54 mm/h intensity led to finer 'raindrops' compared to 39 mm/h. Subsequently, there may have been more kinetic energy in the 39 mm/h event, leading to different mobilisation. Specialist equipment not available for this study could be used in further investigations to determine the kinetic energy in the rain drops of each of the intensities.

4.4.4 Heavy Metal Concentration

Metal concentrations from the samples were shown generally not to vary with time, with Pb the only metal that did vary. It is a possibility that the density of the Pb is the cause of this. As Pb is the densest of the metals, sediment particles with larger amounts of Pb attached may be heavier than those with less. Therefore, it may have taken a greater cumulative volume to transport any of this mobilised sediment. However, it is more likely that this is due to the natural variation in conditions, especially given Pb was the only metal to vary.

For the majority of the metals (5 of the 6), the concentration showed variation with intensity. Cu did not show variation, which is likely to be a result of random natural variation, such as varying concentrations on the sample spaces.

Subsequently, of the 5 metals, 4 showed no significant difference between the 39 and 54 mm/h intensities, and all 5 showing that the lowest intensity (24 mm/h) gave the lowest concentration. One possibility for this is that the lower intensity mobilised less of the pollutants built up on the car park surface. Once again, this is likely a result of the kinetic energy of the droplets, and of that required to mobilise the sediment.

Another possibility is that the lower intensity mobilised the same as the other intensities, but did not transport the pollutants to the same extent. From the

results obtained, this would most likely be attributed to the volume of runoff. Volume was shown to vary with intensity, with the 24 mm/h significantly different to the 39 and 54 mm/h which were not. This would explain the general trend throughout the metal concentrations, where the majority followed this format.

The fact that the concentrations from the 39 and 54 mm/h events were not significantly different suggests that there is a 'threshold' intensity, falling between 24 and 39 mm/h. This would be the point at which more pollutants start to be mobilised, due to increased mobilisation, transportation once mobilised, or both.

4.4.5 Comparison to Reference Values

In order to put the values of the metal concentrations obtained into perspective, they have been compared to Contaminated Land Exposure Assessment (CLEA) 2009 Soil Guideline Values (SGV). The SGV, and the mean value of the metals analysed and recorded in Table 4.3 below. From the CLEA SGV, the 'Commercial' values have been used for comparison, as it is these that the sample sites more closely identify with.

Table 4.3: Comparison of Metal Conc.to CLEA 2009 SGV

Metal	CLEA 2009 SGV (mg/kg)	Mean of Analysed Conc. (mg/kg)
Cu	130	173.84
Ni	1800	26.93
Pb	750	81.99
Cd	230	0.5
Zn	300	446.96
Cr	5000	42.98

It can be seen that the mean metal concentration for Cu and Zn is above the CLEA SGV, with the other four metals concentration falling well within the SGV.

This shows that in general, car parks have relatively low levels of heavy metal pollutants when compared to what is considered safe exposure with regards to contaminated land. For the metals outside the SGV, this is likely due to the specific sources of Cu and Zn that car parks are subjected to, as identified previously.

4.4.6 Effect of Intensity on Characteristics of Mobilised Sediment

A potential 'threshold' between the 24 mm/h intensity, and the 39/54 mm/h intensities was identified for several of the parameters investigated. This may be due to the Capacity Factor (Cf) of the rainfall, which is the capacity of the rainfall to mobilise sediment and pollutant from a surface. This was investigated by Egodawatta (2007) and Liu et al. (2015). Egodawatta (2007) reported that the Cf of rainfall intensities up to 40 mm/h was 0 – 0.5, 40 – 90 mm/h – approximately 0.5, and > 90 mm/h – 0.5 – 1.

These findings would explain the results obtained in this experiment. For example, the 24 mm/h event, which generally gave lower concentrations/mass, would have a Cf of 0 – 0.5. Assuming the 39 and 54 mm/h intensities fall into the 40 – 90 mm/h bracket (variation was shown in calibration as to make the assumption that 39 mm/h is representative of 40 mm/h), they would have a Cf of 0.5. Therefore, the increased capacity for mobilisation of sediment and associated pollutant would explain the result obtained.

Egodawatta and Goonetilleke (2008) suggested that the Cf was primarily affected by rainfall intensity, and density of particles as opposed to their size (Hvitved-Jacobsen et al., 2010). This further explains the results obtained, in particular the lack of variation in Pb with intensity. As Pb is the densest of the metals (11.34 g/cm^3, compared to 8.65, 7.19, 8.96, 8.902 and 7.133 g/m^3 for Cd, Cr, Cu, Ni and Zn respectively (Davis, 1997)) this would suggest that a higher Cf is needed for mobilisation, above that of the rainfall intensities studied, thus no variation occurred. A lack of mobilisation due to this may also explain the generally low Pb concentrations analysed.

4.4.7 Correlation

When analysed, the correlation between particle size (d50) and metal concentration was shown to be ‘very weak’ based on the definition by (Evans, 2006). It has been widely reported that, in highway runoff with smaller particle sizes generally show higher concentrations of metals (Herngren et al., 2006; Dong and Lee, 2009), due to the increased surface area compared those with larger PSD for a given volume.

It is possible that these results are due to agglomeration of particles, meaning that ‘larger’ particles are actually a number of smaller particles. If this were the case, the larger particles would have the higher concentration of pollutant, as they would inherit the sum of the constituent smaller particles. Agglomeration of particles is likely to occur during the build-up of sediment on the car park surface, where they are resident for the time between rainfall events.

Another possibility is that the range of particle sizes acquired by rainfall runoff process is too small to demonstrate this trend. It is possible that given a larger range of intensities, different particle sizes may be mobilised, i.e. the energy from the intensities in this study have kinetic energy too similar to each other to provide a range of particle sizes.

4.4.8 First Flush

One of the objectives of this study was to determine whether a ‘first flush’ of pollutants occurred in runoff entering a channel drain. This is, to say, an initial higher load of pollutants, caused by a prior build up in the period since prior wash-off from a rainfall event.

If a first flush had occurred during the study, a peak in mass and/or pollutant concentration would have been expected over one of the time periods. The results show that neither parameter was shown to vary with time, so therefore no first flush effect was demonstrated.

It is unlikely that the reason for a lack of first flush was insufficient time for it to take effect. This is because by definition, first flush comes from the initial stages of runoff. The results show that sediment and associated pollutants have been washed off. Therefore, further wash-off should not be considered as initial, or ‘first’.

The only way in which a first flush could have occurred, is in the event of a greater influx of sediment/pollutant in the first 5 minutes, with a lower than average amount in the remainder of the 10 minute interval. This is deemed to be unlikely, given no variation was shown throughout the whole duration of the sampling.

This could be examined further by shorter time periods, but as detailed in the Results section, for lower intensities, no runoff was generated in the first 5 minutes, hence the first measurement period was 0 – 10 minutes.

Although a first flush has been demonstrated multiple times (Deletic and Maksimovic, 1998; Wicke, 2009) it is not universally accepted. Bach (2010) argue that the number of variables affecting concentrations makes it difficult to see a general trend. Therefore, although a first flush effect was not demonstrated in this study, the number of variables may account for this, and a repeat study may differ.

4.4.9 Relevance to Legislation

The Draft National Standards for SUDS (2015) suggest that the first 5 mm of runoff should be stored on site, and not discharged, due to the potential pollutants. From the results of this study, 5mm would have fallen at 12.5, 7.7 and 5.6 minutes for the 24, 39, and 54 mm/h intensities respectively.

If this was to be substantiated based on the results of this study, mass and/or pollutant concentration would have peaked at the 20 minute measurement for 24 mm/h, and the 10 minute measurement for 39 and 54 mm/h, the points at which 5mm of runoff would be generated. The results show that neither

parameter was shown to vary with time, so therefore there does not appear to be a higher pollutant load in the first 5mm of runoff based on this study.

4.4.10 Comparison to Highways

Although using a rainfall simulator, this study was intended to be representative of actual rainfall events affecting a car park. Crabtree et al. (2006) covered a range of natural rainfall events, and thus presumably covered a wide, representative range of intensities. Therefore, comparing the results obtained in this study with Crabtree et al. (2006) will indicate whether they are representative of natural rainfall. Table 4.3 displays the results of this study to those obtained by Crabtree et al. (2006).

Table 4.3 Comparison of Results With Highways Study (Crabtree, 2006)

		Results			Crabtree	
		Min. Conc. (mg/kg)	Max. Conc. (mg/kg)	Avg. Conc. (mg/kg)	Max. Conc. (mg/kg)	Avg. Conc. (mg/kg)
Metals	Cd	0.00	1.70	0.49	5.40	0.61
	Cr	2.23	174.05	46.90	49.90	9.36
	Cu	7.46	543.78	163.85	242.00	60.59
	Ni	1.84	118.46	29.44	40.00	8.48
	Pb	6.82	212.95	88.72	178.00	26.54
	Zn	28.71	1742.94	610.94	688.00	205.30

There was a greater range of values obtained in this study, and for all metals but Cd, the maximum concentration was higher. The average values also followed a similar trend. This is likely due to the intensities used in this study, being relatively high, compared to Crabtree et al. (2006) which encompassed all rainfall events. Despite this, the average concentrations are all in the same order of magnitude.

It can also be observed that the average concentrations reported by Crabtree et al. (2006) all fall within the range of values from this study. This suggests that

the runoff from a car park is similar to that of a highway. It also suggests that the methodology of using a rainfall simulator is robust, and comparable to rainfall events.

4.5 Conclusion

Rainfall intensity was shown to generally have an effect on the chemical characteristics (heavy metal concentrations), but not the physical characteristics (particle size) at the intensities studied.

The effect on metals concentrations was shown to be non-linear, with variation generally shown between the low intensity and the two higher intensities, but not between the higher intensities themselves. This is likely due to Capacity Factor (Cf), the capacity of a given rainfall intensity to mobilise sediments pollutants.

Time was shown not to have an effect on the physical or chemical characteristics of the runoff. Therefore, no first flush effect was demonstrated in the runoff generated from the intensities studied.

4.5.1 Further Work

The key limitation of the study was the inability to simulate lower rainfall intensities, more representative of the common events in the UK. Therefore, further work would be recommended using a purpose built rainfall simulator, as with the other studies mentioned throughout, in order to get the desired intensity. The unique element from this study of capturing the runoff entering the channel drain could then be applied.

Additionally, more samples could be taken, on more sites. This would require greater resources, and committed partners on the sample sites in order to aid with logistics, such as providing thousands of litres of water to refill the water butts.

5 Assessment of Wet Vac Sediment Collection Method as a Representation of Rainfall

This paper is prepared as a short communication to a journal such as Science of the Total Environment.

The following communication bridges the two preceding chapters, which cover the accumulation and transport phases of the Conceptual Model. The validity of the sampling method used to collect accumulated sediment is compared to rainfall events, demonstrating which process affects characteristics.

Source → Accumulation → Transport → Treatment

The objective of this communication is to: 'Validate the wet-vac method as representative of a rainfall event.'

5.1 Introduction

The 'wet-vac' method of collecting sediment from urban areas has been utilised extensively. Studies including those by Bris et al. (1999), Deletic and Orr (2005) and Kayhanian et al. (2012) used the method, and as such, a version of this was used in *Chapter 4* as the main sampling methodology. Analysis of the effectiveness of the method has been reported as 95 % by Kayahnian et al. (2012), which is interpreted as collection of 95 % of particles on the highway/carpark surface.

Additionally, the use of simulated rainfall has been used successfully in studies such as Herngren (2005), Egodawatta (2007), Egodawatta (2008) and Egodawatta (2009). It was also used in *Chapter 5* of this study to determine the characteristics of runoff entering a channel drain.

Whilst the high level of collection efficiency of the wet vac method reported by Kayhanian et al., (2012) is of great use in determining what builds up and remains on a paved surface, it is unknown if this is representative of what washes off in a rainstorm. As documented in *Chapter 5*, analysing the actual

runoff is logistically rather difficult, requiring either labour intensive or highly weather dependent manual sampling, or expensive autosamplers. The aim of investigating runoff into channel drains posed extra complications to those of, for example, a drainage ditch, due to the smaller size.

Therefore, this objective of this study is compare the characteristics of samples taken from the 'wet-vac' method, to those collected in runoff in order to determine whether the method is representative of sediment transported by runoff generated from a rainfall event.

5.2 Methods and Materials

5.2.1 Sample Collection

Samples for the 'Runoff' were those documented in *Chapter 5,* obtained by the use of a rainfall simulator as a source of rainfall, and captured via an interceptor placed in a channel drain. These are referred to as "Wash-off".

Samples for the 'wet-vac' were taken in accordance with the methodology described in *Chapter 4.* The samples were taken at the same time as those in *Chapter 5*, and were taken from a 50 x 50 cm area at the edge of the bunded area.

5.2.2 Analytical Methods

The following analytical methods were used in the analysis of the samples. Comprehensive descriptions of these methods are detailed in *Appendix A.*

5.2.2.1 Particle Size Distribution

A MasterSizer 2000 (Malvern Instruments, Malvern, Worcestershire) was used to measure the particle size distribution. This is done by the Fraunhofer diffraction theory, and light scattered from the sample is measured on a series

of detectors. Where possible, analysis took place on the day of collection to prevent agglomeration of particles. In the instance this was not possible, the samples were shaken daily until analysis could be completed.

5.2.2.2 Heavy Metal Concentration

In order to analyse the metal content of the samples, they were first finely ground and 0.5g digested with aqua regia (2 ml HNO_3, 6 ml HCL) in a Perkin Elmer microwave system. Copper, nickel, lead, cadmium, zinc and chromium concentrations were then determined using an atomic absorption spectrophotometer (AAnlayst 800, Perkin Elmer Ltd, Waltham, Massachusetts).

5.2.3 Statistical Analysis

The results from both analyses of the two sets of samples were analysed using a Two Sample T-Test Assuming Equal Variation, using both RStudio Version 0.98.1103 – © 2009-2014 (RStudio, Inc, 2015), and Microsoft Excel (Microsoft, 2015).

5.3 Results

5.3.1 Particle Size Distribution

The results of the particle size and heavy metal concentrations are shown in Table 5.1 below. In order to compare the particle size distribution of the samples, the d50 value was used, as in previous chapters. This is the median particle size (i.e. 50 % of particles are smaller in diameter than d50), and is used in order to characterise the sample. For the ‘wash-off’, an average was calculated for each run, i.e. the 30 minute ‘Sample’ corresponding to the wet-vac sample.

Table 5.1: d50 Values from 'Wet vac' and 'Wash-off Sampling Methods

	d50 (µm)	
Sample	Wet Vac	Washoff
1	44.87	64.71
2	71.43	84.67
3	87.86	111.76
4	89.10	92.38
5	102.09	108.23
6	99.11	93.18
7	117.46	134.01
8	137.68	136.54
9	65.98	85.60
Mean	90.62	101.23
SD	26.28	22.30

The t-test showed that there was no significant difference in the mean of the two sample sets (p = 0.7110). An unpaired T-test was applied, as despite sample locations being adjacent to each other, it was not possible to collect runoff from the area that had been wet-vacuumed, as this removed the sediment.

5.3.2 Heavy Metals

The results from the heavy metal analysis are shown in Table 5.2 below. As per *Chapter 5*, the data provided is the concentration (mg/kg or µg/kg), not the mass. This is because it is accepted that due to slight variance in the sampling, it is more effective to compare characteristics (concentrations) rather than absolute amounts.

All of the metals analysed showed no significant difference between 'Wet Vac' and 'Wash-off' sampling methods (p = 0.3126, 0.1160, 0.0545, 0.6572, 0.2908 and 0.0709 respectively).

Table 5.2: Metal Conc. from 'Wet Vac' and 'Wash-off' Sampling Methods

	Cu (mg/kg)		Ni (mg/kg)		Pb (mg/kg)	
Sample	Wet Vac	Washoff	Wet Vac	Washoff	Wet Vac	Washoff
1	84.23	286.98	26.75	9.18	85.43	24.44
2	89.69	272.35	34.63	24.46	120.92	118.10
3	129.80	83.80	42.60	13.26	152.00	57.00
4	81.32	31.67	24.78	7.36	65.73	35.82
5	125.37	96.50	26.99	32.17	88.38	108.47
6	140.72	102.34	29.54	17.78	115.37	69.10
7	102.58	26.09	35.46	6.43	123.62	23.84
8	101.12	140.87	36.84	43.22	85.70	107.48
9	76.32	199.82	34.97	51.81	75.52	80.71
Mean	103.46	137.82	32.51	22.85	101.41	69.44
SD	22.00	90.58	5.50	15.48	26.34	34.73

	Zn (mg/kg)		Cd (mg/kg)		Cr (mg/kg)	
Sample	Wet Vac	Washoff	Wet Vac	Washoff	Wet Vac	Washoff
1	222.75	127.21	548.50	207.60	49.10	13.40
2	579.18	1194.26	693.49	761.32	54.85	51.17
3	689.60	603.42	955.00	163.08	83.40	24.21
4	332.07	157.56	326.87	2.05	38.36	14.45
5	260.95	775.31	319.54	348.73	52.79	56.23
6	480.04	442.53	459.68	401.81	51.50	32.08
7	500.90	100.38	0.20	231.96	44.28	7.79
8	351.02	470.52	771.13	767.81	54.27	63.51
9	296.90	367.21	629.97	544.09	50.35	65.11
Mean	412.60	470.93	522.71	380.94	53.21	36.44
SD	148.89	333.10	268.03	250.71	11.76	21.52

5.4 Discussion

The statistical analysis showed that none of the parameters tested were significantly different whether the sample had been collected via the ‘wet vac’ method, or as runoff. Zinc was deemed to be ‘Not quite significantly different’, with p = 0.0545). This is most likely due to the greater variance (S.D. = 333.10) compared to other metal concentrations (S.D. = 21.52 – 268.03).

With these results, it could be suggested that the ‘Wet Vac’ method is not only effective as a sampling method in investigation of surface build up, but also that it is representative of the wash-off process.

Furthermore, with the ‘Wash-off’ values taken over a range of rainfall intensities (19 mm/h – 54 mm/h), it can be suggested that the ‘Wet Vac’ method is representative over a range of rainfall events. However, with the results of *Chapter 5* determining that there is no significant difference between the intensities in question, this is not surprising.

It could be argued that the methods show no significant difference due to the large variation for each parameter. However, it is apparent that variation occurs in both groups. This is not unusual, with similar levels of variation occurring in results from *Chapter 5* and this study. When all of the many potential factors influencing pollutants/variety of sources are considered, it is not unexpected.

5.5 Conclusion

The results of the assessment show that there was no significant difference between the physical (PSD) and chemical (heavy metal concentration) characteristics of samples obtained by the ‘wet-vac’ method, and those obtained from sampling runoff. Therefore, it can be concluded that the ‘wet-vac’ method is a viable method of collection a sample representative of runoff.

6 Biodegradation of PAH in Channel Drain Sediment

This paper is prepared in the format for submission to The Science of the Total Environment Journal, or alternatively a conference proceeding.

This paper relates to the final phase of the Conceptual Model, 'Treatment'. The previous papers have identified the potential sources of pollutants, the real-world characteristics of accumulated sediment, and the subsequent transport into the channel drain. It is in this chapter that potential treatment of these pollutants is identified, and investigated.

Source → Accumulation → Transport → Treatment

The objective of this paper is to: 'Identify potential evidence for the biodegradation of PAH in channel drain sediment.'

6.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are identified as one of the major sources of urban pollution, and as such are classified as Priority Pollutants by the EU (EU, 2000). They are deposited from a wide range of sources, including tyres, vehicle emissions, brakes, highway materials and road materials (Thorpe and Harrison, 2008; Mostafa et al., 2009; Dong and Lee, 2009; Bjorkland, 2011). The effects of PAH on the environment have the potential to be devastating.

Degradation of PAH may occur by a number of processes: adsorption, volatilisation, photolysis and chemical degradation. However, biodegradation, the breakdown of compounds by microrganisms, has been identified as the main process by which PAH degrades (Haritash and Kaushick, 2009).

The process of biodegradation has been identified as a possible form of treatment in SUDS. Several studies (Pratt et al., 1999; Newman et al., 2004, 2005) have studied the effects of biodegradation in pervious pavements, generally finding that reduction of PAH concentration occurred. This was

developed further by Puehmeier (2005, 2013), who used a floating mat with an oil degrading biofilm in infiltration systems to further increase biodegradation.

Although similar treatment has not been considered in channel drains, there may be the potential for it to occur. It has been observed (Lundy et al., 2014) that channel drains retain sediment, and it is within this that biodegradation may occur.

A study by SNIFFER (2008) conducted an experiment in which soil from roadside SUDS was spiked with PAH, and the degradation observed over 60 days. The results generally showed a reduction in concentration over the incubation time period, suggesting that there is the potential for biodegradation of PAH in these conditions. The effect of treatments including variations in pH, temperature, moisture content and PAH concentration were observed, as these are known to affect biodegradation (Leahy and Colwell, 1990).

The sediment in channel drains comes from similar sources to that used in (SNIFFER, 2008), and as such, it may provide a similar medium for treatment.

Therefore, the objective of this study is to quantify the microbial degradation of PAH in channel drain sediment. The methodology is based on that of SNIFFER (2008) study, albeit using sediment extracted from channel drains. In doing this, the results can be compared, and more generally channel drains compared to established forms of SUDS, with the possibility of suggesting channel drains are as effective as accepted SUDS at treatment of sediment.

6.2 Methodology

6.2.1 Sample Sediment Collection

Sediment for the experiment was collected from a channel drain on the university campus. The metal covers were removed and approximately 10 kg of built up sediment removed with a Nalgene scoop, and stored in a soil collection bucket at 4 ˚C until preparation and analysis.

6.2.2 Incubation Methodology

The methodology used for the experiment was based on SNIFFER (2008), which used sediment from green SUDS, in order to enable comparison of results. This involved spiking soil samples with a known concentration of PAH (Sigma Aldrich PAH Mix A, 500µg, 13 compounds dissolved in DCM), and then incubated. Variations in the incubation were introduced, including temperature, concentration of PAH and moisture content of the soil.

Slight changes were made with regards to the spiking procedure, as Brinch et al. (2002) determined a superior method, applying the pollutant to 25 % of the soil, and then adding the remaining 75 % once the solvent had dissolved. This was done in order to reduce the proportion of soil subjected to the solvent (acetone), in order to minimise the effect on the indigenous microorganisms.

First, the samples were dried at 30 ˚C for 24 h, and stored at 5 ˚C. Half of the sediment was then sterilised by autoclaving at 121 ˚C at 103.4 kPa for 15 minutes. Sediment was then weighed out into 48 x 25 g samples (24 sterilised and non-sterilised), of which 75 % (18.75 g) was removed and stored. The sample bottles used were amber glass, in order to prevent the effects of light exposure, such as photolysis of the PAH.

Moisture content (by mass) of the samples was then adjusted to 40 %. A mixture of 13 constituent PAH dissolved in acetone (Sigma Aldrich EPA 525 PAH Mix B) was then applied to the sub sample, which was shaken to mix. The bottle lid was then left on for 5 minutes in order for the pollutant to dissipate, and then removed for 16 h to allow evaporation of the acetone. The remaining 75 % of the sediment was then added, the lids put on, and the entire sample was shaken to mix. This meant that each sample received approximately 15 mg/kg of PAH. Once the samples had been spiked with PAH, they were incubated at a constant temperature of 15 ˚C.

In addition to the ‘Control’ condition, detailed above, several treatments were introduced to further batches of samples. The first of these was variation in temperature. Whereas the ‘Control’ samples were kept at 15 ˚C, these were

kept at 4 ˚C, in order to simulate the cool seasonal temperature that the sediment would be subject to in the real world. Secondly, moisture content was doubled, to 80 %, in order to replicate wet and dry periods associated with channel drains. Finally, PAH concentration was doubled, representing a situation such as an influx of PAH after a storm event.

Six bottles (3 sterilised and non –sterilised) were then removed at 0,1,3,7,14,28,42 and 60 days after treatment (DAT), and stored at -60 ˚C in order to prevent any further degradation until all samples had been taken and analysis took place.

6.2.3 Analytical Methods

Samples were removed from frozen storage and left to defrost overnight in a refrigerator, as to minimise further degradation. Once defrosted, ultrasonic sequential extraction took place.

For the PAH analysis of the samples, they were first extracted by ultrasonic sequential extraction using a method based on (Risdon et al., 2008). Firstly, 5.0 g +/- 0.1 g of sample, and also an equal amount of Na_2SO_4 was weighed out and manually blended with the sediment in order to remove moisture. The sample was then transferred to a centrifuge tube and 1 ml of 100µg/ml surrogate standards were added and allowed to equilibrate for 12hrs at 20^{o}C.

6 ml of DCM was added, and the sample sonicated for 2 minutes at 20^{o}C. 10 ml hexane and 4 ml DCM were then added, and the sample sonicated for 10 minutes, then manually shaken. Samples were then centrifuged for 5 minutes at 750 rpm, then passed through a filter column with the filtrate retained.

The residue was re-suspended in 10 ml Hexane:DCM mix (1:1), sonicated for 15 minutes at 20^{o}C and centrifuged for 5 minutes at 750 rpm. The sample was then filtered through a filter column with the filtrate retained. This was then repeated, and the final extract made up to 40 ml with a Hexane:DCM mix (1:1).

The extract was then cleaned up using Sigma SPE-18 Solid Phase Extraction cartridges. Once done, 900 µl of sample and 100µl of the deuterated PAH mix was transferred to a GC-MS vial.

The sample was then analysed using an Agilent GC-MS, using the 'alkane.std' program.

The full analytical method used is detailed in *Appendix A.*

6.2.4 Statistical Analysis

An unpaired T-test was applied to the results obtained from the experiment. This was carried out using GraphPad Ystat (2015).

6.3 Results

6.3.1 Explanatory Note

Unfortunately, 127 of the 192 samples were contaminated/destroyed. All of the samples were extracted and analysed using the methods described above. However, when the results of the GC-MS analysis were interpreted, a lack of PAH was displayed. The analysis was repeated several times, with blanks and standards for quality control, but no data was obtained, despite the machine functioning correctly.

It is believed that during storage at -18 ˚C, the freezer was left open, the samples defrosted, and the PAH in the samples was lost, due to its volatile nature. Due to the expense of analysis, and time constraints, it was not possible to repeat the experiments.

The results of the successful samples have been used in this chapter, however it is acknowledged that these are unfortunately, and unavoidably lacking in number and depth.

6.3.2 Results Table

Results of the three replicates for each sample were averaged, the results of which are recorded below.

Table 6.1: PAH Conc. Over 60 Day Incubation Period

	Condition							
	Control		Temperature		Moisture Content		PAH Conc.	
DAT	Non-Sterilised	Sterilised	Non-Sterilised	Sterilised	Non-Sterilised	Sterilised	Non-Sterilised	Sterilised
0	-	-	2.1747	1.66	2.59	2.51	3.57	3.91
1	-	-	1.65	-	1.78	2.66	3.55	1.7
3	-	-	2.1	1.42	1.62	2.53	3.46	2.11
7	-	-	2.83	1.59	1.61	2.14	2.7	1.68
14	-	-	-	-	-	2.26	-	2.24
28	-	-	-	-	-	-	-	-
42	-	-	-	-	-	-	-	-
60	-	-	-	-	-	-	-	-

Table 6.2: % Reduction of PAH Concentration

	% Reduction	
Variable	Non-Sterilised	Sterilised
Temperature	30.13	-4.22
Moisture Content	-37.84	-9.96
PAH Conc.	-24.37	31.76

6.3.3 Graphs

Graphs of the results were plotted in Figure 6.1 in order to show the concentration of PAH over time under the different conditions. Error bars were added to show standard deviation.

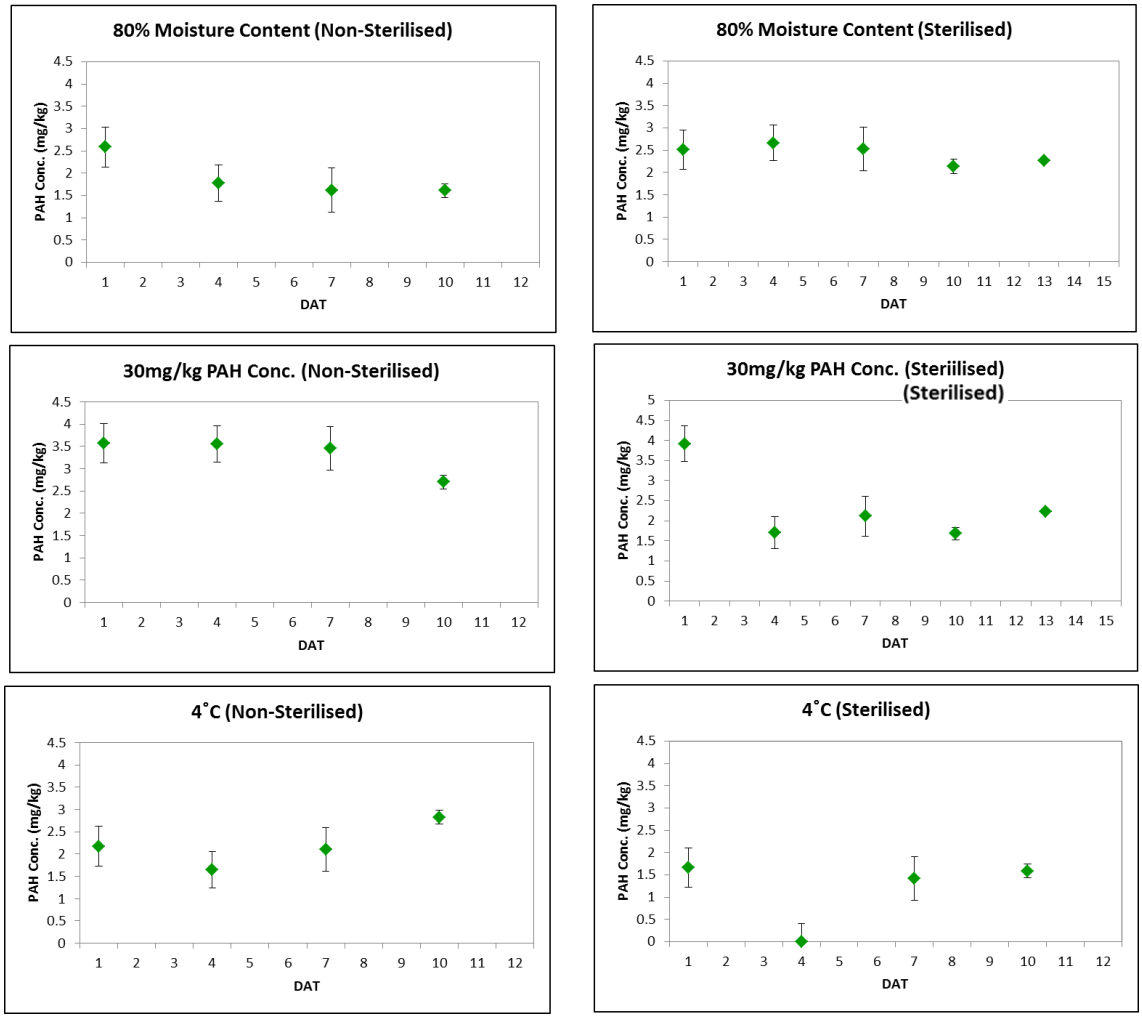

Figure 6.1: PAH Conc. Over Incubation Period

6.3.4 Control

Samples from the 'Control' condition were destroyed as per 6.*3.1.*

6.3.5 Moisture Content Variable

The results from the samples from the 'Moisture Content' condition (4 ˚C, 80 % moisture content, 15 mg/kg PAH) showed a net reduction for both the sterilised and non-sterilised samples. The trend shown by the sterilised samples is smoother, with an initial drop from days 0 - 1, then no further noticeable reduction.

On the other hand, the non-sterilised samples show a more erratic trend, as they barely change over the first sample days, with the mean fluctuating until 3 DAT, when there is a drop before a final rise.

No significant reduction was shown by the sterilised samples ($p = 0.5444$), whereas the reduction by the non-sterilised samples was deemed to be 'not quite significant' ($p = 0.0788$).

The difference the reduction of PAH between the non-sterilised and sterilised samples was shown to be statistically significant ($p = 0.0443$).

6.3.6 Temperature Variable

The results from the samples from the 'Temperature Variable' condition (4 ˚C, 40 % moisture content, 15 mg/kg PAH) show no real discernible trend for either the non-sterilised or sterilised sample batches. Concentrations fluctuated throughout the incubation period.

No significant reduction in PAH concentration occurred for either the non-sterilised or sterilised samples ($p = 0.3982$ and $p = 0.8355$ respectively).

The difference between the PAH concentration reduction between the non-sterilised and sterilised samples was shown to not statistically significant ($p = 0.0841$).

6.3.7 PAH Concentration Variable

The results from the 'PAH Concentration' condition (15 ˚C, 40 % moisture content, 30 mg/kg) showed a net reduction in PAH concentration for both non-sterilised and sterilised samples. The trend in reduction differed, with the non-sterilised samples showing little/slight reduction over the first 3 sample dates, with a greater reduction by the final day, whereas the sterilised samples had an initial drop in concentration on the first sample date, and fluctuated with net increase for the remaining time period.

The reduction in PAH concentration was shown to be significant in the non-sterilised ($p = 0.0133$) but not the sterilised samples ($p = 0.6798$) over the time period.

The difference between reduction in PAH concentration between the non-sterilised and sterilised samples was shown to be 'not quite statistically significant' ($p = 0.0841$).

6.4 Discussion

6.4.1 Biodegradation

It is immediately apparent that the concentration of the PAH at 1 DAT varies widely. Whereas the soil samples were initially spiked at 15 mg/kg, the resulting values ranged from as low as 1.51 mg/kg – 3.91 mg/kg. This was despite following the method set out by Brinch et al. (2008). This was also observed by SNIFFER (2008). In the study, two causes were suggested: volatilisation, and an initial surge in microbial breakdown. It was concluded that a surge in biodegradation was the cause, however, their spiking procedure involved less time for solvents to evaporate, with a higher risk of damage to microbes. It is therefore suggested that volatilisation was the main contributor in this study.

With the exception of those under the temperature condition, a reduction was seen in the PAH concentration over the time period. The reduction in concentration in the sterilised samples was shown to be non-significant under every condition, whereas the non-sterilised samples showed a significant (or nearly significant) reduction in the majority of cases. This would suggest that biodegradation is at least in part responsible for the reduction of PAH concentration in channel drain sediment, as measures were taken to prevent degradation by other forms.

Despite this, the argument that biodegradation is the only, or indeed main, form of breakdown cannot be made. This is due to the observations made regarding the concentration of PAH at 0 DAT. The highest recorded values were

approximately 6 - 7 times less than those applied to the soil samples. This implies that breakdown or removal occurred in whilst the samples were left to shed solvent residue. During this time, it is possible this was due to photolysis, or most likely volatilisation.

6.4.2 Effect of Treatments

6.4.2.1 Temperature

Both the non-sterilised and sterilised results from the temperature condition were rather erratic. No significant reduction in concentration displayed, with a decrease of 4 % in the sterilised samples and in fact an increase (30 %) in the non-sterilised samples. The fact that this happened to both is interesting, as it suggest that biodegradation as not a factor, as the behaviour was similar, unlike that of the other conditions, in which the non-sterilised samples were shown to have a more significant effect.

Unfortunately, the control samples were destroyed, and thus unavailable for comparison, but the results from the other treatments at the control temperature suggest that microbes are functional at 15 ºC. With the results having suggested against biodegradation effecting a reduction in PAH concentration at 4 ºC, it would seem inappropriate to suggest it as a treatment in a real world scenario, as lower temperatures are prevalent in this country.

6.4.2.2 Moisture Content

Ideally, the results would have been compared to those of the ‘Control’ moisture content (40 %) in order to establish whether the increase had an effect on biodegradation. By interpreting the results of the other treatments, and the fact degradation was exhibited, it can be said that biodegradation can occur at 40 % moisture content, at least that it is not the limiting factor.

A reduction in PAH concentration was shown within the 80% moisture content samples, albeit deemed as ‘not quite statistically significant’. However, given the

limited data set, it is likely that with more data points, this would have been significant. Therefore, it could be suggested that it is possible for biodegradation to occur at both lower and higher moisture contents.

The reduction in PAH from the non-sterilised samples (38 %) was shown to be more significant than that of the sterilised samples (10 %). This suggests that biodegradation is occurring, and responsible for the reduction in PAH concentration.

6.4.2.3 PAH Concentration

Whilst it is not possible to compare the samples containing higher PAH concentrations to the control samples, it is shown that reduction occurred in both the non-sterilised (24 %) and sterilised (42 %) samples. The non-sterilised samples showed a steady degradation across the sample period, whereas the sterilised samples exhibited a sharp drop between DAT 0 and 1, with fluctuating values thereafter. It is possible that the initial sample is an anomaly, based on what has already been discussed regarding volatilisation of the samples upon spiking. With this removed, the sterilised samples actually show an increase of 32 % in concentration.

With this applied, the concentration reduction in the non-sterilised samples was shown to be significant, whereas that of the sterilised samples was shown not to be. This suggests that biodegradation has occurred.

6.4.3 Comparison to SNIFFER

A key difference between the two studies was the initial drop experienced in the SNIFFER (2008) study. Whereas a substantial drop occurred between 0 and 1 DAT in several of their results, it appears this happened before the initial sampling (0 DAT) in this study. Once again, the extended time allowed for solvent evaporation is suggested as the cause of this.

Discounting the initial drop between 0 and 1 DAT, the results as a whole behave in a similar way to those in the SNIFFER (2008) study. In several instances for both studies, concentrations showed a net reduction over the entire period, whilst rising in between, particularly in the earlier stages. It is likely that this is due to the volatile nature of the PAH, and the spiking process, with varied volatilisation rates upon application effecting differing initial values.

6.4.4 Comparison to green SUDS

It is clear that despite showing a net reduction in most instances, that there is insufficient scope to categorically state that channel drains behave in the same way as established ‘green’ SUDS. However, the fact that the concentration of PAH did decrease over time, and similar trends were shown to sediment from green SUDS, suggests that they may be comparable. Further work would be needed to confirm this.

6.5 Conclusion

Although the data in this study is unfortunately limited, it is still possible to suggest a number of conclusions. These are reinforced by the similar SNIFFER (2008) study, which, as alluded to in the *Discussion* section, which had similar results.

A key conclusion that can be drawn is that the results suggested that biodegradation of PAH may occur in channel drains. The non-sterilised samples generally showed more significant reduction in PAH concentration than the sterilised equivalents. However, there is simply not enough data, or strong enough evidence to prove this beyond doubt.

One of the main aims of the study was to determine whether channel drains were able to provide treatment in a way similar to that of established Green SUDS. Although under the circumstances this could not be proved, the fact that the results obtained were similar to those in the SNIFFER (2008) report is

promising. Given that significant reduction was shown despite problems and subsequently a small dataset, it is possible that the full results would have followed the trend.

The sizeable drop in PAH concentration between application of spiking solution and the 0 DAT samples must involve ‘treatment’, as the PAH concentration in the sediment reduced. There are two possibilities for this: volatilisation, and rapid biodegradation.

Whilst SNIFFER (2008) determined that this was caused by initial rapid degradation, this study disproves this, by exhibiting the same scale of drop in both the non-sterilised and sterilised samples. If the cause had been biodegradation, the sterilised samples would not have exhibited the same loss, due to a lack of microbes. From this, it could be said that treatment is occurring in channel drains, just not with biodegradation as the primary mechanism.

With regards to the treatments imposed on the samples, it is difficult to draw any firm conclusions, due to the failure of the ‘Control’ batch for comparison. The only suggestion that can be made is that colder temperature (4 ˚C) had a noticeable effect. This was displayed by no significant reduction in concentration in the non-sterilised samples, and an erratic trend in the sterilised batch, suggesting a reduction in volatilisation rate.

As an overall conclusion to the study, it is suggested that biodegradation is not a viable form of treatment in channel drains. Whilst the results show that there was a general reduction in PAH concentration over the time period, the effectiveness varied greatly. In summary, biodegradation of PAH may occur in channel drain sediment, however, it is not reliable, or quantifiable enough to prescribe as a treatment method.

6.5.1 Further Work

Although the study suggested the potential for biodegradation in channel drain sediment, the amount of data meant it was inconclusive. Further work could

involve repeating the experiment, and obtaining the full data set needed, in order to quantify any treatment, and determine whether treatment is taking place.

The study could also be repeated in a ‘real world’ experiment, by monitoring the PAH concentrations in in-situ channel drains over a time period. This would show whether treatment of PAH occurs in channel drain sediment under non-laboratory conditions.

7 Integrated Discussion

The experimental work in the previous chapters was undertaken in order to answer the research questions initially posed, and to achieve the aim set. The findings from the experimental work are discussed below, by combining those relevant to each research question.

7.1 Research Question 1

Are the physical and chemical characteristics of the sediment that enters channel drains on car parks during rain-storms of different intensities the same as that of the sediment found on the car park surface?

7.1.1 Particle Size Distribution

The median particle size, d50, was used to compare the particle size distribution of sediments. The average d50 of sediment found on car park surfaces was 85.87 µm +/- 5.18 µm, and that of the samples obtained from the runoff entering a channel drain was 100 µm +/- 9.1 µm. These are not statistically different from each other, showing that characteristics of the sediment build-up on car park surfaces retains the same physical characteristics when washed off by rainfall.

This was further supported by the d50 of the sediment washed off by simulated rainfall (*Chapter 6*) which showed no significant difference to samples obtained by the wet-vac method on an adjacent plot. This shows that median particle size does not change throughout the process of build-up and wash-off. This suggests that rainfall at the intensities investigated does not preferentially wash off particular particle sizes from the sediment found in in car park surface build-up.

7.1.2 Metals

The concentrations of a selection of 6 heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) were analysed in surface build-up in *Chapter 4*, wash-off in *Chapter 5*, and from both in *Chapter 6.* As with the particle size, the results from wash-off vs. wet-vac samples in *Chapter 6* are not statistically different to each other. This suggests that the chemical characteristics of the sediment remain the same from build-up through the process of wash-off into the channel drain.

The above observation is further supported by comparison of the metal concentrations between the wash-off from *Chapter 5* and the entire results of the wet-vac sampled build-up from *Chapter 4*. The range of both sets of results is detailed in Table 7.1 below.

Table 7.1 Metal Concentrations from 'Wet Vac' and 'Wash-off'

	Metal					
	Cd (µg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
WV Min.	0.20	16.00	36.00	13.00	0.00	161.00
R Min.	0.00	2.23	7.46	1.84	6.82	28.71
WV Max.	170.00	202.00	301.00	70.60	334.00	1868.00
R Max.	1699.84	174.05	543.78	118.46	212.95	1742.94

WV = Samples acquired by Wet-vac method

R = Samples acquired by Rainfall simulation

It can be seen from the results that the range of results were broadly similar for both the build-up and wash-off. In 5 out of 6 cases, the wash-off minimum concentration was lower than that of the build-up. This may be down to the natural variation within car parks, as the results are not dissimilar, and most certainly in the same order of magnitude.

Another likely reason for the lower values is the effect of rainfall on them. It was quite clearly established in *Chapter 5* that the intensity had an effect on the majority of metals, with the 24 mm/h generally leading to a lower metal

concentration in the washed off sediment. This would explain the slightly lower values when compared to wet vac.

The only metal that displayed lower concentrations between the 2 studies was Pb. This is explainable by the concentrations below LOD, and a known limitation of the AAS analytical method.

The maximum concentrations from each sampling method/study were also similar, although there was more variation between them which provided the higher concentrations. Once again, this is most likely due to natural variation between the sample sites.

In summary, given the number of sources of pollutants, and the variation within the range of concentrations for each metal, it can be concluded that the methods produce similar results.

7.2 Research Question 2

Do the physical and chemical characteristics of the sediment found on car park surfaces differ significantly with type of use and location and how do they compare with highway sediments?

7.2.1 Particle Size Distribution

The physical characteristics of car park sediment was analysed in *Chapters 4* and *5* in the form of surface build-up and wash-off respectively. The average particle size (d50) values from both studies were not significantly different, so they can be compared to those reported from highways. Poleto et al. (2009) and Deletic and Orr (2005) reported d50 values ranging from 26 – 122 µm and 86 – 369 µm respectively. Values from *Chapters 4* and *5* displayed ranges from 39 – 144 µm and 42 – 142 µm, with averages of 86 and 100 µm respectively. It can be seen from these that the physical characteristics of car park sediment build-up and wash-off is not dissimilar to that of highways.

These findings are not unexpected, as despite differing potential factors affecting the pollutants on both, the sources are fundamentally similar. This means that from the perspective of physical characteristics, car parks can be regarded in the same way as highways, using the extensive body of research into the latter to inform decisions.

7.2.2 Metals

When compared to a number of similar studies, the samples taken from the wet-vac method in *Chapters 4* and *6* were shown to correspond closely with results obtained from highway studies (Robertson et al., 2003; Carraz et al., 2003; Gunawardana et al., 2012; Wei and Yang, 2012). Similarly, the results of the rainfall study were consistent with the results of Crabtree et al. (2006), who analysed the runoff from a number of storm events, with the averages falling within the range of results obtained in this present study.

Given that both of these sampling methods returned similar values to corresponding studies based on highways, it can be concluded that with regard to the chemical characteristics of car park sediment are comparable to that of highways. Several possible reasons have been identified over the course of the project as to why both uses may be different (number of vehicles, residence time of vehicles, surrounding infrastructure etc.), The reason for these not effecting differences between the car parks and highways, is most likely the natural variation due to varying sources, leading to a wide range of concentrations for each metal, cancelling out the effect of the other variables.

In terms of potential treatment, this means that the literature on highways may be credible in the context of car parks.

7.3 Research Question 3

Are the physical and chemical characteristics of the runoff entering the environment from channel drains the same as those of the water entering the drains?

7.3.1 PAH

PAH was analysed in *Chapter 4,* where its concentration in car park sediment build-up was analysed, and *Chapter 5,* where their degradation in channel drain sediment was quantified. The results of the analysis of car park sediment showed generally low values, ranging from 0 – 10,300 µg/kg, with over a third returning no detectable PAH. In the biodegradation of PAH in channel drain sediment experiment (*Chapter 7*), a higher concentration was used to spike the sediment, in line with other studies to enable comparison.

Despite the PAH biodegradation study providing limited data with regards to the initial aim, it does explain the results of the car park surface sediment samples, discussed in the next section

The main part of the project dealing with the potential treatment in channel drains was the PAH degradation study in *Chapter 7*. Unfortunately, the results from this were limited, due to accidental destruction of many of the samples. The results obtained did show some of reduction in PAH concentration under certain conditions, although there was insufficient data to show a significant reduction due to biodegradation.

The majority of samples in *Chapter 4* returned low, or negligible levels of PAH. Although this was not necessarily out of line with similar studies, that so many of the results were below the LOD, or barely detectable, given the number of potential sources identified, was unexpected.

Meanwhile, the key observation from the biodegradation study in *Chapter 7* was that the majority of the 15 mg/kg of PAH used to spike the samples disappeared before the first samples were taken at DAT 0. It was likely that the PAH had

been broken down in that time, due to biodegradation, photolysis, or more likely volatilisation.

This reduction was exhibited in the 12 hours the samples were left to acclimatise after spiking with PAH mix. It was therefore concluded that treatment of PAH in channel drains is possible, just not necessarily primarily due to biodegradation. Large amount of sediment build-up were observed in channel drains throughout the study, therefore it is reasonable to assume that in most cases, sediment is retained long enough for these processes to occur. It is this rapid reduction in PAH concentration that may explain the low concentrations/lack of PAH found on car parks.

The concentration of PAH in sediments deposited on car parks is likely to be lower than the 15 mg/kg used to spike the channel drain sediment, based on deposition sources. Any PAH on the car park surface is also likely to be spread out more i.e. on an open space as opposed to in a sample bottle. As a result, this is likely to exacerbate the effect of volatilisation of PAH, and also the possibility of photolysis on exposure to light. It could be said that this means that PAH is not important with regards to treatment, as it seems to be broken down before reaching the channel or other receptor. However, it could also be argued that this does in fact constitute a form of treatment, as any PAH deposited from the various sources appears to have been ‘treated’.

7.3.2 Heavy Metals

Heavy metals cannot be treated in the same way as PAH as they accumulate rather than degrade.

This is reflected in the current accepted forms of Sustainable Drainage Systems (SUDS). The SUDS Manual (CIRIA, 2007) is a comprehensive guide to the forms and uses of SUDS in the UK. For each forms of SUDS, it attributes performance characteristics such as amenity, storage and relevant to this study – treatment. The main forms of SUDS used in order to provide treatment are swales, infiltration basins and soakaways. All of these facilitate treatment by

filtration, either using the ground in infiltration basins, or sized aggregate and membranes in soakaways. The difference between these and channel drains, is that the SUDS are designed to attenuate volumes of runoff as well as treat, whereas channels are designed only to convey runoff.

From this study, two potential methods for treating metals deposited on car park surfaces can be suggested. Firstly, in a similar way to PAH above, the build-up of sediment on the car park (in the 'pore spaces') could be classed as treatment, as it retains sediment, meaning it is not in the channel of receiving sewers/watercourses. The results of *Chapter 4* demonstrated that the sediment on car parks does in fact contain retained pollutants.

The second of these is the build-up of sediment in channel drains, which was observed throughout the study. Once again, this works on the principle that if the sediment, and hence pollutants, are in the channel, they are prevented from reaching sewers/receiving watercourses, effecting treatment providing they are eventually removed from the channel, as detailed below.

7.3.3 Development of Treatment Mechanisms

With this knowledge, car park surfaces can be considered to provide treatment of urban pollutants. This could be developed in order to potentially increase treatment. For example, 'pore spaces' in the tarmac could be increased, in order to retain more sediment, and subsequently subject it to the effects of volatilisation/photolysis. This could also enable 'treatment' of heavy metals, by retaining them, preventing to transport to the channel drain, and discharge to sewers/watercourses.

The other suggested form of treatment, in the channel drains themselves, would require the retention of sediment. This would 'treat' metals and PAH by retention, therefore allowing them to degrade/volatilise. In order to increase the effectiveness, the channel would have to be altered in order to retain more sediment, through methods such as baffles or filtration media. The problem with this, is the reduction in volume, and thus primary function – conveyance of

water. It is likely that the sizes would have to be increased in order to deal with extra capacity. This would have to be modelled and developed accordingly.

Importantly, if this method of treatment was to be implemented, a strict maintenance routine would be required to remove sediment before it affected the conveyance of water. This is in line with other forms of SUDS, such as swales, which have documented maintenance routines (CIRIA, 2007).

7.3.4 Physical factors affecting treatment

Throughout this study, several aspects of urban pollution have been studied: build-up on car park surfaces, wash-off into a channel drain, and treatment within the channel. These have been the quantifiable aspects of treatment and have taken place in ‘controlled’ conditions.

A number of observations have been made about car parks and their pollutants. These are the physical factors of car parks, which, although non-quantifiable, may have an effect on the behaviour of pollutants, and subsequent treatment.

During *Chapter 4,* several observations were made whilst vacuuming the car parks. Firstly, the variability of sediment amount among car parks/car park spaces. Although this was determined by tactile/visual examination, some spaces appeared relatively devoid of sediment, whereas others appeared to be covered. This was particularly evident where the spaces were near to planted areas/exposed soil.

Proximity of the space to built features such as kerbs or walls also had an effect, presumably due to the obstruction of runoff flow and subsequent ponding. This was also the case for the channel drains themselves. It was noted on several occasions that the sides/grate of a channel drain was raised, up to a maximum of around 10mm, effecting similar consequences as kerbs/walls. This may have been a result of poor installation, or settlement of the surrounding car park.

Furthermore, the topography of car parks seemed to exacerbate the uneven distribution of sediment. Where there were lower sections – possibly from underlying ground/settlement – there tended to be greater build-up, which may have resulted from ‘ponding’ of water during rainfall.

It could be argued that these factors make accurate characterisation of car park pollutants difficult. However, given the amount of variation found in the results of studies, and the variable nature of pollutant sources, car park characteristics, rainfall etc., it is likely that the results obtained portray an accurate representation of the characteristics of car park pollutants. The methodology also addressed these points, with random sampling, and a number of replicates.

8 Conclusion

8.1 Conclusions

1. Both the physical and chemical characteristics of car park surface build up were shown to be similar to those of highways. Particle size, heavy metal concentrations and PAH concentrations were shown to fall within the range of values reported from a number of similar studies investigating the build-up on highways. As a result of these findings, the extensive literature relating to highway pollution could be used and applied to further research on car park pollutants.

2. Rainfall intensity was shown to generally have an effect on the chemical characteristics of runoff (heavy metals), but not the physical characteristics (particle size) at the intensities studied. The effect on metals was shown to be non-linear, with variation generally shown between the low intensity and the higher intensities studied, but not between the higher intensities themselves.
   Time was shown not to have effect on the physical or chemical characteristics, and as such, a first flush effect was not demonstrated for the intensities and time studied.

3. The ‘wet-vac’ method developed to sample surface build-up was shown to be representative of rainfall events over the range of intensities and duration studied, with the physical and chemical characteristics showing similarity.

4. The potential for treatment of PAH through the process of biodegradation in channel drain sediment was demonstrated, but not comprehensively proved. However, the potential for treatment of PAH in channel drain sediment as a whole was demonstrated, with concentrations reducing greatly and rapidly due to probable factors such as volatilisation and photolysis.

5. The physical and chemical characteristics of sediment were shown not to vary between build-up on a car park surface, and that washed off into a channel drain. This suggests that the sediment and associated pollutants on a surface are washed off wholly and non-preferentially.

8.2 Overall conclusion

The overall aim of the project was:

To determine the physical and chemical characteristics of sediments found on car parks in the UK and the changes in those characteristics between the car park surface and the environment.

Overall, it has been demonstrated that the physical and chemical characteristics of the sediment build-up on car parks remain the same throughout the wash-off process. This was shown by the characteristics of the build-up in *Chapter 4* being comparable to that washed off into a channel drain in *Chapter 5.*

Furthermore, it can be concluded that the physical and chemical characteristics of both the build-up and wash-off from from car parks is no different to that of highways. The build-up was shown to be comparable to studies concerning highways in *Chapter 4*, and subsequently the wash-off from simulated rainfall showed the same with the runoff entering a channel drain in *Chapter 5.*

Finally, it can be concluded that channel drains, and similar engineered drainage products do have the potential to facilitate treatment of urban pollutants.

This is based on two main factors. Firstly, the observation at different points throughout the project that channel drains almost always had a build-up of sediment within them. This is due to presence of the sediment, as retention in a channel means it is not entering a sewer or receiving watercourse. It was shown comprehensively in *Chapter 4* and *5,* that the sediment built-up on, and

subsequently washed off a car park surface into a channel drains, contains level of pollutant, similar to those on highways. If the sediment is contained within the channel, the associated pollutants will be too. Therefore, through a reduction in pollutants entering and leaving the channel, treatment process can be determined to have taken place.

The potential for further treatment of pollutants, PAH, within the sediment was also demonstrated. A reduction in PAH concentrations was demonstrated, with spiked concentrations reducing by over 5 times over a period of 12 hours. It was not possible to show this was as a result of biodegradation, and it was deemed likely that this was due to volatilisation. By retaining sediment in the channel, and the associated PAH, a medium would be provided for volatilisation to take place, reducing the concentration of PAH, and therefore effecting a treatment in the channel.

Although the potential for treatment in channel drains and engineered drainage products has been identified, it is evident that development would be necessary in order for them to function to the same level as established SUDS counterparts, such as swales. The purpose of channel drains at present is to convey water, and in fact avoid sediment build-up, in order to maintain an unobstructed flow. If they were to be developed to form part of the SUDS treatment train, it would be necessary to make modifications to optimise performance. These may include measures such as the inclusion baffles, of filtration media in order to slow the flow, and encourage deposition of sediment. This would impact on the effectiveness of the channels primary purpose, to convey water, as flow rates would be reduced. This would most likely necessitate an increase in size of channel to compensate, however this is still likely to facilitate a smaller land take than equivalent ‘green’ SUDS.

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APPENDICES

Appendix A: Overview of Analytical Methods

A.1 General Sediment Sample Preparation Procedures

The method for the reception and preparation of samples for the project was as detailed below for all subsequent analyses, unless stated otherwise. This was based on Cranfield University *SOP 1 – Sample Receipt, Storage, Preparation, Stone content and Disposal,* which in turn was based on British Standard BS 7755: Section 2.6:1994 *Guidance on the collection, handling and storage of soil for the assessment of aerobic microbial processes in soil,* which is identical to ISO 10381-6:1993, British Standard BS ISO 11464:2006 *Pretreatment of sample for physico-chemical analyses.*

Upon reception, samples were labelled using a standard form including: Study Identifier, Client Identification, Sample Type and Number, and Date of Receipt.

A.1.1 Storage of Sediments Prior To Analysis

Air dried samples were stored at room temperature.

Moist samples (soil or sediment) were kept in unopened containers at 4 ˚C in a refrigerator.

A.1.2 Storage of Water Samples Prior to Analysis

Water samples were kept in unopened containers at 4 ˚C in a refrigerator.

A.1.3 Sample Preparation of Soils and Sediments

Soil and sediment samples were air dried by breaking large pieces up in to smaller pieces, and placed into a drying tray. These were then placed onto a

drying rack, inside a drying cupboard. Samples were checked regularly, with larger pieces broken up further when necessary.

For soil and sediment suspended in water, an initial method of filtration was attempted, in order to reduce the time taken to air dry, due to the large ration of water to sediment. This was ultimately unsuccessful, with filtration taking a long time, and the water required to wash the sediment from the filter paper excessive due to its stickiness.

Air dried samples were then ground, in order to pass through a 2mm sieve. Grinding was done by a mechanical grinder, for a period of 1 minute. The resulting material was then passed through a 2mm sieve, and stones/other material in the > 2mm fraction was discarded.

A.1.4 Preparation of Water Samples

Water samples remained refrigerated at 4 ˚C throughout the project.

A.1.5 Disposal of Soil, Sediment, and Plant Material

Once the sediment had been used/analysed, samples were either stored for potential future analysis, or disposed of to landfill.

A.1.6 Disposal of Water Samples

Once the water samples had been used/analysed, they were poured down the sink, and diluted with large quantities of water.

A.2 Particle Size Distribution

The method for analysis of Particle Size Distribution (PSD) of samples was based on Cranfield University *SOP 111, which* sets out a method for the use of a Mastersizer 2000 (Malvern Instruments, Malvern, Worcestershire).

Samples of sediment suspended in water were passed through a 2mm sieve in order to remove stones, and other > 2mm materials, which are too large for the Mastersizer, and not of interest.

The Mastersizer was set up to take a 'Manual' measurement, rather than a pre-loaded SOP.

The machine was set up following the on screen instructions, to calibrate and align the optics.

Measurement options were set, including material (sample) description in order to set the refractive index, measurement (set to 15 seconds), and measurement cycles (3 cycles with the average calculated).

Obscuration limits were left at 25 % default, as the samples contained a broad range of particle sizes.

A HydroMU unit was used to feed sample into the Mastersizer for analysis, with a pump speed of 1250.

Samples were shaken to ensure a representative sample was analysed, and immediately poured into a 600 ml beaker, in which the HydroMU stirrer was situated.

Sample was added until the onscreen obscuration bar fell into the green 'acceptable' section.

Once analysed, the 'Results Analysis' tab was selected. This tab allowed the laser response to be examined, in order to check accuracy. It was checked that 'Weighted Residual' was less than 3 %, and that a response of < 20 was obtained at receptor 20 to reduce noise from a potentially unclean optic.

The beaker of sample was transferred back into the sample container for the next analysis.

The process was repeated for all of the samples, and the data exported.

Upon finishing, the system was rinsed through with water, and the Mastersizer optic cleaned.

A.2.1 Quality Control

Samples were analysed as shortly as possible after acquisition. Where this was not possible, samples were shaken daily in order to prevent agglomeration of particles.

Samples bottles were shaken before being decanted into the HydroMU in order to get a representative sample.

Several replicates were analysed, and the average calculated to account for slight variations.

The Mastersizer optics were cleaned every 10 samples, in order to prevent the build-up of particles, which may have led to false obscuration.

'Weighted Residual' was checked for each sample to be < 3 %, in order to ensure a good fit of data.

A response of < 20 at receptor 20 was ensured, in order to reduce noise and inaccuracy from residue in the sensor.

A.3 Heavy Metals Analysis

The method used to determine the concentrations of heavy metals is described below. This is based on Cranfield University SOP 17 – *Determination of Elements Soluble in Aqua Regia*, which itself is based on British Standard BS 7755:Section 3.13:1998, which is identical to ISO 11047:1998, and USA EPA Method 3051.

A.3.1 Overview

A hydrochloric/nitric acid mixture was used to extract the sample using a microwave digestion system. Extracts were then filtered, and made up to volume with water. Atomic absorption was then used to determine the metal content of the extracts.

A.3.2 Atomic Absorption Spectroscopy

Soil/sediment samples were prepared as per the method in *3.1*.

0.5g +/- 0.001g of sediment was weighed out in to a labelled microwave digestion liner.

6 ml +/- 0.1 ml of 1.18 specific gravity hydrochloric acid, and 2 ml +/- 0.1 ml of 1.42 specific gravity nitric acid was added to the liner using dispensers. The liner was then swirled to mix, and left for pre-reactions/gas formations to reside.

The liner was then placed into a pressure vessel, with the cap screwed on hand-tight.

This was repeated for all of the samples, which were then placed into the microwave rotor. Samples were evenly spaced in order to keep the unit balanced. One ‘Blank’ sample was also added, containing only the acid mixture.

Sample vessel number ‘1’ was sealed with the p/T sensor accessory in order to measure parameters during digestion. The seal was expanded using the seal forming device, hand tightened to the ‘Stop’ position, and then reopened by around 60˚.

The lid was the placed onto the rotor and it was placed into the microwave, and the fume hood was activated.

The microwave was then set to run using the appropriate SOP – ‘NR-SAS SOP 17’.

Once the microwave digestion was complete, the rotor was removed, and placed in a fume hood to cool. Once cool, the vessels were opened with the vent pointing into the fume hood.

The samples were then filtered through a Whatman 542 filter into separate 100 ml volumetric flasks. The liners and seal were rinsed into the appropriate samples, which were then made up to 100 ml with deionised water.

Once complete, the samples were transferred to plastic bottle for storage.

A.3.3 Determination of Metals by Flame Atomic Absorption

Calibration curves were prepared using the relevant standard working solutions.

The sample extracts were then measured using a Perkin Elmer Flame atomic absorption unit (PerkinElmer Ltd, Waltham, Massachusetts).

In order to calculate the concentration of the original sample from the analysis of the extract, the following formula was used:

$$\text{mg/kg metal}^{x} = \frac{(M^{x}_{a} - M^{x}_{b}) \times 100 \times D}{m_1}$$

where

- M^{x}_{a} is the concentration, in µg/ml, of metal^{x} in the sample extract;
- M^{x}_{b} is the concentration, in µg/ml, of metal^{x} in the blank extract;
- D is a dilution factor;
- m_1 is the mass, in grams, of sample taken for digestion.

Figure A.1: Formula for Determination of Sample Metal Conc (Cranfield University SOP 17 – *Determination of Elements Soluble in Aqua Regia)*

A.3.4 PAH Analysis

The method for analysis of PAH was based on Cranfield University *SOP - Extraction Of Total Petroleum Hydrocarbon (TPH) & Polycyclic Aromatic Hydrocarbon (PAH) In Soil By Gas Chromatography,* which itself was based on the method of sequential ultrasonic solvent extraction detailed by Risdon et al. (2008).

A.3.5 Standards

Frozen soil samples were defrosted overnight in a refrigerator at 4 ˚C. Upon defrosting, any water on the surface of the sample was discarded.

A.4.1.1 Sequential Ultrasonic Solvent Extraction

5.0g +/- 0.1g of the defrosted soil, and 5.0g +/- 0.1g of Na_2SO_4 was weighed out into a Nalgene centrifuge tube (rinsed with DCM), and blended with a stainless steel spatula.

1 ml of 100 µg/ml surrogate standard was added, and the samples left to equilibrate at 20 ˚C for 12 hours.

6 ml of DCM was added to the samples, which were then sonicated at 20 ˚C for 2 minutes.

10 ml of Hexane, and 4 ml DCM was added, and samples were sonicated for 10 minutes at 20 ˚C.

Samples were then centrifuged for 5 minutes at 750 rpm.

The liquid was passed through a filter column, with the filtrate retained in a centrifuge tube.

10 ml of 1:1 DCM:Hexane was added to the leftover residue.

The sample was sonicated for 15 minutes at 20 ˚C, then centrifuged for 5 minutes at 750 rpm.

The liquid was once again decanted through a filter column and retained.

The previous three steps were then repeated.

The extract was then made up to 40 ml with a mixture of 1:1 DCM:Hexane.

A.4.1.2 Sample Clean Up

6 ml of extract was passed through a DSC-18 SPE cartridge, and collected in a centrifuge tube.

900 µl of extract and 100 µl of deuterated PAH standard was then transferred to a GC vial.

A.3.6 GC\MS Analysis

3 µl of sample was analysed by an Agilent GC-MS using the *'Alkane.std'* method.

The GC vials containing extract were then analysed immediately as below, or stored at -18 ˚C until analysis.

A.4.2.1 Quality Control

PAH standards of 1 µg/ml were analysed every 20 samples.

Blank samples consisting of DCM:Hexane 1:1 were run at randomly space intervals.

Appendix B: Investigation Into the Physical and Chemical Properties of Channel Drain Sediment

B.1 Output from Statistical Analyses

B.1.1 ANOVA Results

D50

```
  Df Sum Sq Mean Sq F value   Pr(>F)
Location    13  18281  1406.3   5.116 7.14e-06 ***
Residuals   56  15394   274.9
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

TPAH

```
            Df    Sum Sq  Mean Sq F value Pr(>F)
Location     7 115922446 16560349   5.308 0.0015 **
Residuals   20  62396078  3119804
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
17 observations deleted due to missingness
```

Cd

```
            Df   Sum Sq Mean Sq F value Pr(>F)
Location    13 11553949  888765   26.28 <2e-16 ***
Residuals   56  1893629   33815
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Cr

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Location    13  19001  1461.6   4.265 6.47e-05 ***
Residuals   56  19189   342.7
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Cu

```
            Df Sum Sq Mean Sq F value Pr(>F)
```

```
Location    13 323980   24922   56.48 <2e-16 ***
Residuals   56  24710     441
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Ni

```
            Df Sum Sq Mean Sq F value Pr(>F)
Location    13  41829    3218   1.535  0.134
Residuals   56 117351    2096
```

Pb

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Location    13 213166   16397   19.59 9.33e-16 ***
Residuals   53  44374     837
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
3 observations deleted due to missingness
```

Zn

```
            Df   Sum Sq Mean Sq F value Pr(>F)
Location    13 10107503  777500   61.17 <2e-16 ***
Residuals   56   711741   12710
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

B.1.2 LSD Test Results

D50

```
Study: d50$d50 ~ d50$Location

LSD t Test for d50$d50

Mean Square Error:  274.9

d50$Location,  means and individual ( 95 %) CI

  d50.d50       std r      LCL       UCL   Min    Max
A  87.484 22.635041 5 72.63027 102.33773 71.60 127.41
B 107.742 16.232450 5 92.88827 122.59573 84.43 123.20
C  88.186 11.280897 5 73.33227 103.03973 78.07 101.00
D  73.148 12.905292 5 58.29427  88.00173 62.31  93.04
E  74.052  3.014726 5 59.19827  88.90573 71.86  79.20
F  84.652 13.850602 5 69.79827  99.50573 70.94 103.21
G  76.462 17.755183 5 61.60827  91.31573 62.67 106.49
H 104.062 22.509938 5 89.20827 118.91573 71.60 131.62
I 102.646 17.147991 5 87.79227 117.49973 79.47 127.00
J  85.068 18.423201 5 70.21427  99.92173 65.43 104.69
K  60.150 17.669203 5 45.29627  75.00373 39.33  79.64
L  60.088  6.242862 5 45.23427  74.94173 52.44  67.40
M  83.694 18.383130 5 68.84027  98.54773 60.86 104.41
N 114.756 20.817138 5 99.90227 129.60973 90.94 143.51

alpha: 0.05 ; Df Error: 56
Critical Value of t: 2.003241

Least Significant Difference 21.00635
Means with the same letter are not significantly different.

Groups, Treatments and means
a        N       114.8
ab       B       107.7
abc      H       104.1
abc      I       102.6
bcd      C       88.19
bcd      A       87.48
cd       J       85.07
cd       F       84.65
cd       M       83.69
de       G       76.46
de       E       74.05
de       D       73.15
e        K       60.15
e        L       60.09
```

TPAH

```
Study: TPAH$TPAH ~ TPAH$Location

LSD t Test for TPAH$TPAH

Mean Square Error:  3119804

TPAH$Location,  means and individual ( 95 %) CI

  TPAH.TPAH       std r        LCL      UCL  Min   Max
A    6232.5 1279.6451 4  4390.2848 8074.715 5450  8140
B    6075.0 2631.2545 4  4232.7848 7917.215 3040  9130
C    2440.0 1325.5188 4   597.7848 4282.215 1180  4200
D    1690.0        NA 1 -1994.4303 5374.430 1690  1690
E    7240.0 2315.6856 4  5397.7848 9082.215 5040 10300
F    2824.5 1875.0825 4   982.2848 4666.715  598  4780
G    2260.0  900.7219 3   132.7932 4387.207 1730  3300
H    2555.0 1030.2912 4   712.7848 4397.215 1560  3870

alpha: 0.05 ; Df Error: 20
Critical Value of t: 2.085963

Minimum difference changes for each comparison

Means with the same letter are not significantly different.

Groups, Treatments and means
a        E       7240
a        A       6232
a        B       6075
b        F       2824
b        H       2555
b        C       2440
b        G       2260
b        D       1690
```

Cd

```
Study: cd$Cd ~ cd$Location

LSD t Test for cd$Cd

Mean Square Error:  33815

cd$Location,  means and individual ( 95 %) CI

     cd.Cd       std r        LCL       UCL     Min     Max
A  395.506 143.77728 5  230.76457  560.2474  152.97  533.93
B  773.916  82.34632 5  609.17457  938.6574  687.00  901.44
C  419.940 234.01444 5  255.19857  584.6814   20.24  597.88
D 1179.132  84.33277 5 1014.39057 1343.8734 1043.13 1243.65
E  515.862 447.32802 5  351.12057  680.6034   25.25  926.91
F 1099.820 186.92188 5  935.07857 1264.5614  872.15 1355.03
G  677.746 181.08279 5  513.00457  842.4874  385.14  879.40
H 1607.630 194.57487 5 1442.88857 1772.3714 1304.61 1762.93
I 1075.084 208.92911 5  910.34257 1239.8254  833.90 1376.05
J  410.136  62.31447 5  245.39457  574.8774  367.68  519.70
K  324.206  98.01579 5  159.46457  488.9474  188.20  424.78
L  326.200  98.11462 5  161.45857  490.9414  246.70  494.61
M  419.726  93.90908 5  254.98457  584.4674  324.10  533.27
N  137.858  52.91654 5  -26.88343  302.5994   95.10  229.70

alpha: 0.05 ; Df Error: 56
Critical Value of t: 2.003241

Least Significant Difference 232.9796
Means with the same letter are not significantly different.

Groups, Treatments and means
a        H       1608
b        D       1179
b        F       1100
b        I       1075
c        B       773.9
cd       G       677.7
de       E       515.9
e        C       419.9
e        M       419.7
e        J       410.1
e        A       395.5
ef       L       326.2
ef       K       324.2
f        N       137.9
```

Cr

```
Study: cr$Cr ~ cr$Location

LSD t Test for cr$Cr

Mean Square Error:  342.7

cr$Location,  means and individual ( 95 %) CI

   cr.Cr       std r      LCL       UCL   Min    Max
A 67.446  2.903503 5 50.86139  84.03061 64.68  70.99
B 72.352  7.416186 5 55.76739  88.93661 64.20  83.73
C 57.384  3.159119 5 40.79939  73.96861 54.23  62.63
D 46.932  4.674342 5 30.34739  63.51661 42.17  53.12
E 54.216  5.571493 5 37.63139  70.80061 47.49  60.87
F 64.106  3.438972 5 47.52139  80.69061 59.07  68.51
G 95.846 59.957996 5 79.26139 112.43061 60.60 202.70
H 55.754  1.914910 5 39.16939  72.33861 53.31  58.12
I 60.656  5.890440 5 44.07139  77.24061 52.18  65.96
J 48.098  4.858983 5 31.51339  64.68261 42.97  55.01
K 57.510 16.896918 5 40.92539  74.09461 35.61  82.86
L 40.092  7.340328 5 23.50739  56.67661 31.27  50.11
M 81.456 21.994841 5 64.87139  98.04061 62.28 118.13
N 27.372 13.378512 5 10.78739  43.95661 16.07  49.93

alpha: 0.05 ; Df Error: 56
Critical Value of t: 2.003241

Least Significant Difference 23.45418
Means with the same letter are not significantly different.

Groups, Treatments and means
a        G       95.85
ab       M       81.46
bc       B       72.35
bcd      A       67.45
bcd      F       64.11
bcde     I       60.66
cde      K       57.51
cde      C       57.38
cde      H       55.75
cde      E       54.22
def      J       48.1
def      D       46.93
ef       L       40.09
f        N       27.37
```

Cu

```
Study: cu$Cu ~ cu$Location

LSD t Test for cu$Cu

Mean Square Error:  441

cu$Location,  means and individual ( 95 %) CI

    cu.Cu       std r       LCL       UCL    Min    Max
A 188.598 21.182994 5 169.78459 207.41141 161.36 209.58
B 218.304 26.330386 5 199.49059 237.11741 191.40 261.13
C 194.608 14.296481 5 175.79459 213.42141 174.91 211.08
D 174.268 19.546108 5 155.45459 193.08141 145.71 197.28
E 280.034 33.314812 5 261.22059 298.84741 221.44 301.60
F 195.200 10.579327 5 176.38659 214.01341 179.78 206.67
G 231.620 17.572175 5 212.80659 250.43341 208.80 256.76
H 229.402 10.262742 5 210.58859 248.21541 212.22 236.77
I 227.146  9.143964 5 208.33259 245.95941 218.11 239.66
J  96.958  6.780875 5  78.14459 115.77141  88.68 104.21
K 110.830 38.968257 5  92.01659 129.64341  79.04 171.99
L  82.812 19.669041 5  63.99859 101.62541  65.42 109.58
M  64.862  4.834550 5  46.04859  83.67541  60.17  72.50
N  66.596 27.471773 5  47.78259  85.40941  36.21 110.18

alpha: 0.05 ; Df Error: 56
Critical Value of t: 2.003241

Least Significant Difference 26.60617
Means with the same letter are not significantly different.

Groups, Treatments and means
a        E       280
b        G       231.6
b        H       229.4
b        I       227.1
bc       B       218.3
cd       F       195.2
cd       C       194.6
d        A       188.6
d        D       174.3
e        K       110.8
ef       J       96.96
fg       L       82.81
g        N       66.6
g        M       64.86
```

Ni

```
Study: ni$Ni ~ ni$Location

LSD t Test for ni$Ni

Mean Square Error:  2096

ni$Location,  means and individual ( 95 %) CI

    ni.Ni          std r      LCL      UCL   Min    Max
A  49.292    2.5286696 5   8.2769  90.3071 46.85  52.90
B  62.554    5.0064239 5  21.5389 103.5691 58.10  70.60
C  46.854    1.8182217 5   5.8389  87.8691 44.48  49.29
D  48.120    3.8736352 5   7.1049  89.1351 42.97  51.23
E  36.652    0.6023869 5  -4.3631  77.6671 36.07  37.60
F  44.256    9.7108331 5   3.2409  85.2711 30.66  58.07
G 128.438 169.9521067 5  87.4229 169.4531 49.60 432.43
H  47.080    3.8218647 5   6.0649  88.0951 44.36  53.71
I  50.848    5.3154558 5   9.8329  91.8631 44.38  57.56
J  25.700    7.0180909 5 -15.3151  66.7151 13.79  31.91
K  36.566   10.7791386 5  -4.4491  77.5811 24.53  51.66
L  33.520    3.3739517 5  -7.4951  74.5351 28.54  36.04
M  32.082    6.6663498 5  -8.9331  73.0971 27.61  43.68
N  27.060    6.7519923 5 -13.9551  68.0751 17.21  35.12

alpha: 0.05 ; Df Error: 56
Critical Value of t: 2.003241

Least Significant Difference 58.00411
Means with the same letter are not significantly different.

Groups, Treatments and means
a        G       128.4
b        B       62.55
b        I       50.85
```

```
b       A       49.29
b       D       48.12
b       H       47.08
b       C       46.85
b       F       44.26
b       E       36.65
b       K       36.57
b       L       33.52
b       M       32.08
b       N       27.06
b       J       25.7
```

Pb

```
Study: pb$Pb ~ pb$Location

LSD t Test for pb$Pb

Mean Square Error:  837

pb$Location,  means and individual ( 95 %) CI

       pb.Pb       std r        LCL       UCL    Min    Max
A  23.704000 10.135651 5  -2.246974  49.65497  16.62  41.52
B  55.410000 29.070496 5  29.459026  81.36097  36.84 106.77
C  14.978000 13.005425 5 -10.972974  40.92897  -3.80  30.61
D  23.994000 14.310583 5  -1.956974  49.94497   7.90  39.94
E   5.806667  2.562056 3 -27.695897  39.30923   3.00   8.02
F  91.070000 46.180798 5  65.119026 117.02097  60.93 172.55
G  35.942500  4.066181 4   6.928429  64.95657  33.37  42.00
H  83.884000 14.173617 5  57.933026 109.83497  73.53 108.22
I  50.244000  9.531384 5  24.293026  76.19497  39.76  63.37
J  81.140000  3.490902 5  55.189026 107.09097  76.49  85.27
K  87.216000  8.861421 5  61.265026 113.16697  77.16  96.59
L  99.284000 27.840469 5  73.333026 125.23497  71.24 137.96
M 241.150000 61.627836 5 215.199026 267.10097 161.70 334.77
N  84.326000 51.652336 5  58.375026 110.27697  47.20 175.51

alpha: 0.05 ; Df Error: 53
Critical Value of t: 2.005746

Minimum difference changes for each comparison

Means with the same letter are not significantly different.

Groups, Treatments and means
a        M       241.2
b        L       99.28
bc       F       91.07
bc       K       87.22
bcd      N       84.33
bcd      H       83.88
bcd      J       81.14
cde      B       55.41
def      I       50.24
efg      G       35.94
efg      D       23.99
efg      A       23.7
fg       C       14.98
g        E       5.807
```

Zn

```
Study: ZN$Zn ~ ZN$Location

LSD t Test for ZN$Zn

Mean Square Error:  12710

ZN$Location,  means and individual ( 95 %) CI

     ZN.Zn       std r       LCL       UCL     Min     Max
A  783.546 112.27625 5  682.5461  884.5459  656.40  927.12
B 1042.266 168.28829 5  941.2661 1143.2659  844.20 1294.33
C  732.068  81.30211 5  631.0681  833.0679  662.59  865.35
D  783.546 112.27625 5  682.5461  884.5459  656.40  927.12
E 1675.494 117.82915 5 1574.4941 1776.4939 1566.73 1868.64
F  828.198  68.94501 5  727.1981  929.1979  745.31  919.93
G  691.340 135.11218 5  590.3401  792.3399  479.73  851.40
H  961.646 196.93930 5  860.6461 1062.6459  717.03 1214.83
I  957.448  49.92238 5  856.4481 1058.4479  904.10 1005.40
J  317.860  95.40501 5  216.8601  418.8599  233.53  469.55
K  304.228  50.84591 5  203.2281  405.2279  253.50  370.47
L  247.650  52.14766 5  146.6501  348.6499  161.88  291.66
M  414.720  75.17597 5  313.7201  515.7199  308.90  506.63
N  252.230 139.87276 5  151.2301  353.2299  163.25  494.32

alpha: 0.05 ; Df Error: 56
Critical Value of t: 2.003241

Least Significant Difference 142.8354
Means with the same letter are not significantly different.

Groups, Treatments and means
a        E       1675
b        B       1042
bc       H       961.6
bc       I       957.4
cd       F       828.2
d        A       783.5
d        D       783.5
d        C       732.1
d        G       691.3
e        M       414.7
ef       J       317.9
ef       K       304.2
f        N       252.2
f        L       247.6
```

Appendix C: Results: Investigation into the Physical and Chemical Properties of Car Park Surface Build-up

C.1 Full Rainfall Simulator Calibration Data

Calibration 1	
Nozzle	Lechler 402 608 30
Pressure (Bar)	0.45

Run 1		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	155	22.86
2	150	22.12
3	205	30.23
4	135	19.91
5	150	22.12
	Average	23.45

Run 2		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	175	25.81
2	175	25.81
3	165	24.33
4	145	21.38
5	135	19.91
	Average	23.45

Run 3		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	165	24.33
2	175	25.81
3	175	25.81
4	145	21.38
5	155	22.86
	Average	24.04

Calibration 1 Average	**23.65**

Calibration 2	
Nozzle	460-788-17CE
Pressure (Bar)	0.70

Run 1		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	210	30.97
2	205	30.23
3	225	33.18
4	205	30.23
5	210	30.97
	Average	31.12

Run 2		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	210	30.97
2	205	30.23
3	245	36.13
4	205	30.23
5	225	33.18
	Average	32.15

Run 3		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	215	31.71
2	200	29.50
3	235	34.66
4	205	30.23
5	210	30.97
	Average	31.41

Calibration 2 Average	**31.56**

Calibration 3	
Nozzle	460-788-17CE
Pressure (Bar)	1.00

Run 1

Bucket No.	Volume (ml)	Intensity (mm/h)
1	265	39.08
2	255	37.61
3	265	39.08
4	250	36.87
5	275	40.56
	Average	38.64

Run 2

Bucket No.	Volume (ml)	Intensity (mm/h)
1	255	37.61
2	245	36.13
3	275	40.56
4	255	37.61
5	275	40.56
	Average	38.49

Run 3

Bucket No.	Volume (ml)	Intensity (mm/h)
1	265	39.08
2	250	36.87
3	280	41.29
4	260	38.35
5	275	40.56
	Average	39.23

Calibration 3 Average	**38.79**

Calibration 4	
Nozzle	460-788-17CE
Pressure (Bar)	1.50

Run 1

Bucket No.	Volume (ml)	Intensity (mm/h)
1	365	53.83
2	350	51.62
3	375	55.31
4	345	50.88
5	385	56.78
	Average	53.68

Run 2

Bucket No.	Volume (ml)	Intensity (mm/h)
1	360	53.09
2	340	50.14
3	365	53.83
4	345	50.88
5	385	56.78
	Average	52.95

Run 3

Bucket No.	Volume (ml)	Intensity (mm/h)
1	350	51.62
2	345	50.88
3	350	51.62
4	345	50.88
5	390	57.52
	Average	52.50

Calibration 4 Average	**53.04**

Calibration 5	
Nozzle	460-788-17CE
Pressure (Bar)	0.45

Run 1		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	335	49.41
2	305	44.98
3	315	46.46
4	305	44.98
5	325	47.93
	Average	46.75

Run 2		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	300	44.24
2	270	39.82
3	310	45.72
4	310	45.72
5	330	48.67
	Average	44.83

Run 3		
Bucket No.	**Volume (ml)**	**Intensity (mm/h)**
1	310	45.72
2	290	42.77
3	315	46.46
4	305	44.98
5	330	48.67
	Average	45.72

Calibration 5 Average	**45.77**

C.2 Output from Statistical Analyses

C.2.1 D50

Average of d50		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	42.37	78.03	73.73
	2	92.56	92.72	91.86
	3	128.32	128.10	138.19
39	1	71.34	74.04	94.11
	2	105.87	107.89	103.38
	3	141.50	137.16	138.17
54	1	101.11	110.60	114.51
	2	98.16	97.30	91.93
	3	81.27	85.40	86.35

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	263.24	298.855	303.772	865.867
Average	87.74667	99.61833	101.2573	96.20744
Variance	1864.32	662.3958	1104.979	948.6937
1				
Count	3	3	3	9
Sum	318.713	319.0995	335.656	973.4685
Average	106.2377	106.3665	111.8853	108.1632
Variance	1230.673	997.8117	539.5057	699.7938
1				
Count	3	3	3	9
Sum	280.5355	293.307	292.791	866.6335
Average	93.51183	97.769	97.597	96.29261
Variance	114.6382	158.8931	222.2874	128.3099
Total				
Count	9	9	9	
Sum	862.4885	911.2615	932.219	
Average	95.83206	101.2513	103.5799	
Variance	869.5453	470.1345	508.0067	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	851.5699	2	425.785	0.555734	0.583185	3.554557
Columns	284.458	2	142.229	0.185637	0.832145	3.554557
Interaction	138.9148	4	34.72871	0.045328	0.995757	2.927744
Within	13791.01	18	766.167			
Total	15065.95	26				

C.2.2 Volume

Sum of Volume		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	0.10	0.45	0.25
	2	1.10	0.55	0.45
	3	0.15	0.50	1.00
39	1	3.50	3.75	3.20
	2	5.60	7.10	8.55
	3	5.00	6.75	7.45
54	1	2.30	3.30	2.95
	2	6.00	6.10	4.20
	3	4.70	6.10	7.70

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	1.35	1.5	1.7	4.55
Average	0.45	0.5	0.566667	0.505556
Variance	0.3175	0.0025	0.150833	0.120278
1				
Count	3	3	3	9
Sum	14.1	17.6	19.2	50.9
Average	4.7	5.866667	6.4	5.655556
Variance	1.17	3.390833	7.9825	3.702778
1				
Count	3	3	3	9
Sum	13	15.5	14.85	43.35
Average	4.333333	5.166667	4.95	4.816667
Variance	3.523333	2.613333	6.0625	3.19
Total				
Count	9	9	9	
Sum	28.45	34.6	35.75	
Average	3.161111	3.844444	3.972222	
Variance	5.412361	7.885278	10.46694	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	137.4357	2	68.71787	24.52912	7.23E-06	3.554557
Columns	3.423519	2	1.711759	0.611019	0.553678	3.554557
Interaction	2.254259	4	0.563565	0.201167	0.934433	2.927744
Within	50.42667	18	2.801481			
Total	193.5402	26				

C.2.3 Mass

Sum of Mass (g)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	0.24	0.22	0.59
	2	0.08	0.21	0.26
	3	0.04	0.24	0.05
39	1	0.69	0.50	0.50
	2	0.50	1.05	0.50
	3	1.30	1.16	0.51
54	1	0.36	0.29	0.14
	2	0.34	0.36	0.29
	3	1.38	1.36	0.18

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	0.3542	0.6736	0.8936	1.9214
Average	0.118067	0.224533	0.297867	0.213489
Variance	0.010942	0.000107	0.075031	0.02765
1				
Count	3	3	3	9
Sum	2.4931	2.7155	1.516	6.7246
Average	0.831033	0.905167	0.505333	0.747178
Variance	0.174269	0.127247	3.59E-05	0.109318
1				
Count	3	3	3	9
Sum	2.0828	2.0089	0.6128	4.7045
Average	0.694267	0.669633	0.204267	0.522722
Variance	0.352716	0.358501	0.006373	0.236557
Total				
Count	9	9	9	
Sum	4.9301	5.398	3.0224	
Average	0.547789	0.599778	0.335822	
Variance	0.241861	0.21107	0.038166	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	1.292488	2	0.646244	5.262462	0.015865	3.554557
Columns	0.351916	2	0.175958	1.432851	0.264579	3.554557
Interaction	0.425841	4	0.10646	0.866922	0.502597	2.927744
Within	2.210447	18	0.122803			
Total	4.280692	26				

C.2.4 Metals

Cu

Average of Cu (mg/kg)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	543.78	514.29	89.86
	2	18.70	49.19	58.78
	3	17.92	57.81	11.49
39	1	377.91	306.02	269.31
	2	99.00	144.25	94.50
	3	143.80	161.91	187.33
54	1	145.67	99.75	47.88
	2	143.71	124.37	90.11
	3	258.44	198.91	242.03

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	580.4032	621.2904	160.1283	1361.822
Average	193.4677	207.0968	53.3761	151.3135
Variance	92040.21	70793.74	1557.402	46528.02
1				
Count	3	3	3	9
Sum	620.7055	612.1776	551.1388	1784.022
Average	206.9018	204.0592	183.7129	198.2247
Variance	22435.38	7874.881	7649.412	9609.889
1				
Count	3	3	3	9
Sum	547.8185	423.0329	380.0232	1350.875
Average	182.6062	141.011	126.6744	150.0972
Variance	4314.22	2665.737	10426.87	4984.715
Total				
Count	9	9	9	
Sum	1748.927	1656.501	1091.29	
Average	194.3252	184.0557	121.2545	
Variance	29808.54	21377.54	8110.138	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	13555.16	2	6777.581	0.27757	0.760807	3.554557
Columns	28166.36	2	14083.18	0.576765	0.571759	3.554557
Interaction	21298.94	4	5324.736	0.21807	0.924891	2.927744
Within	439515.7	18	24417.54			
Total	502536.2	26				

Ni

Average of Ni (mg/kg)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	17.40	16.46	2.88
	2	4.35	11.44	13.67
	3	4.42	14.25	2.83
39	1	31.68	29.94	24.01
	2	16.47	69.20	26.91
	3	62.11	42.24	46.91
54	1	20.95	17.20	8.26
	2	18.42	17.33	26.49
	3	42.96	33.57	104.81

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	26.16552	42.14424	19.37917	87.68893
Average	8.721841	14.04808	6.459723	9.743215
Variance	56.48402	6.328955	38.96166	36.82731
1				
Count	3	3	3	9
Sum	110.2511	141.3852	97.83175	349.468
Average	36.75036	47.1284	32.61058	38.82978
Variance	540.1063	403.3027	155.4103	316.6559
1				
Count	3	3	3	9
Sum	82.32324	68.10248	139.5577	289.9834
Average	27.44108	22.70083	46.51923	32.22038
Variance	182.1632	88.61534	2631.246	844.7265
Total				
Count	9	9	9	
Sum	218.7398	251.6319	256.7686	
Average	24.30443	27.9591	28.52985	
Variance	347.5222	345.2973	1016.665	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	4184.806	2	2092.403	4.590148	0.0245	3.554557
Columns	94.60977	2	47.30488	0.103774	0.901965	3.554557
Interaction	1285.83	4	321.4576	0.705188	0.598689	2.927744
Within	8205.238	18	455.8465			
Total	13770.48	26				

Pb

Average of Pb (mg/kg)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	46.31	43.79	7.65
	2	21.15	55.64	66.49
	3	16.38	52.83	10.50
39	1	156.96	142.23	114.15
	2	93.17	175.63	110.83
	3	133.50	122.60	120.08
54	1	105.87	63.26	30.36
	2	83.09	92.79	65.98
	3	142.46	89.42	50.59
		88.76	93.13	64.07

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	83.83452	152.2594	84.63534	320.7293
Average	27.94484	50.75314	28.21178	35.63659
Variance	258.5405	38.33424	1100.741	477.9542
1				
Count	3	3	3	9
Sum	383.6335	440.4614	345.0481	1169.143
Average	127.8778	146.8205	115.016	129.9048
Variance	1041.01	718.912	21.96862	637.4436
1				
Count	3	3	3	9
Sum	331.4151	245.4737	146.9302	723.8191
Average	110.4717	81.82457	48.97674	80.42434
Variance	896.9873	261.2817	319.0702	1079.493
Total				
Count	9	9	9	
Sum	798.8831	838.1945	576.6137	
Average	88.76479	93.13272	64.06819	
Variance	2686.666	2056.985	1901.364	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	40022.24	2	20011.12	38.67427	3.05E-07	3.554557
Columns	4421.243	2	2210.621	4.272333	0.030315	3.554557
Interaction	3824.196	4	956.0491	1.847698	0.163698	2.927744
Within	9313.69	18	517.4272			
Total	57581.37	26				

Zn

Average of Zn (mg/kg)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	241.04	227.96	39.83
	2	93.04	244.74	292.46
	3	68.95	222.45	44.21
39	1	1540.71	1529.25	1109.94
	2	842.87	982.14	888.58
	3	586.99	522.05	537.77
54	1	1064.39	707.83	339.74
	2	604.70	625.07	319.10
	3	625.67	399.36	260.20

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	403.0345	695.1465	376.494	1474.675
Average	134.3448	231.7155	125.498	163.8528
Variance	8682.395	134.8287	20911.54	10037.38
1				
Count	3	3	3	9
Sum	2970.567	3033.443	2536.297	8540.306
Average	990.1888	1011.148	845.4323	948.9229
Variance	243672.2	254240.3	83241.43	151395.4
1				
Count	3	3	3	9
Sum	2294.758	1732.259	919.0393	4946.056
Average	764.9194	577.4197	306.3464	549.5618
Variance	67369.95	25491.45	1703.545	63506.99
Total				
Count	9	9	9	
Sum	5668.359	5460.848	3831.83	
Average	629.8177	606.7609	425.7589	
Variance	227536.1	184359.9	131667.3	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	2773788	2	1386894	17.69379	5.63E-05	3.554557
Columns	224800	2	112400	1.433983	0.264321	3.554557
Interaction	163822.8	4	40955.7	0.522507	0.720443	2.927744
Within	1410895	18	78383.06			
Total	4573306	26				

Cd

Average of Cd (mg/kg)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	393.36	372.03	65.00
	2	1.21	3.18	3.80
	3	159.35	514.06	102.16
39	1	860.24	1063.67	740.70
	2	443.97	777.16	-0.59
	3	1227.29	491.89	968.14
54	1	-6.84	390.29	187.33
	2	520.30	501.82	384.23
	3	508.19	697.40	698.71

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	553.9172	889.2717	170.9593	1614.148
Average	184.6391	296.4239	56.98643	179.3498
Variance	38925.2	69536.32	2466.588	38497.19
1				
Count	3	3	3	9
Sum	2531.509	2332.722	1708.246	6572.478
Average	843.8365	777.574	569.4153	730.2753
Variance	153599.1	81734.78	256615.8	138365.9
1				
Count	3	3	3	9
Sum	1021.65	1589.502	1270.278	3881.429
Average	340.55	529.8339	423.4259	431.2699
Variance	90548.36	24167.09	66530.77	52063.99
Total				
Count	9	9	9	
Sum	4107.077	4811.495	3149.483	
Average	456.3418	534.6106	349.9426	
Variance	159786.5	87279.65	133675.1	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	1369161	2	684580.3	7.857459	0.003524	3.554557
Columns	154647.3	2	77323.63	0.887503	0.428946	3.554557
Interaction	108521.3	4	27130.32	0.311396	0.866587	2.927744
Within	1568248	18	87124.89			
Total	3200577	26				

Cr

Average of Cr (mg/kg)		Column Labels		
Row Labels	**Replicate**	**10**	**20**	**30**
24	1	25.39	24.01	4.20
	2	8.53	22.44	26.82
	3	5.35	17.26	3.43
39	1	68.73	62.45	47.92
	2	29.82	120.67	46.31
	3	84.21	62.46	75.62
54	1	40.78	29.70	14.26
	2	39.88	30.88	41.51
	3	60.44	43.06	124.37

Anova: Two-Factor With Replication

SUMMARY	10	20	30	Total
1				
Count	3	3	3	9
Sum	39.27125	63.71731	34.45121	137.4398
Average	13.09042	21.2391	11.48374	15.27109
Variance	115.9403	12.47107	176.5636	96.76245
1				
Count	3	3	3	9
Sum	182.7552	245.5878	169.8494	598.1924
Average	60.9184	81.8626	56.61646	66.46582
Variance	785.3043	1129.652	271.5306	683.4385
1				
Count	3	3	3	9
Sum	141.0999	103.6471	180.1388	424.8858
Average	47.03329	34.54904	60.04625	47.20953
Variance	135.0003	54.70317	3288.984	991.5846
Total				
Count	9	9	9	
Sum	363.1263	412.9522	384.4393	
Average	40.34737	45.88358	42.71548	
Variance	713.1151	1060.573	1485.15	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	12035.31	2	6017.654	9.071613	0.001885	3.554557
Columns	138.8834	2	69.44171	0.104683	0.901154	3.554557
Interaction	2095.102	4	523.7755	0.789591	0.546978	2.927744
Within	11940.3	18	663.3499			
Total	26209.59	26				